

STATUS OF DIFFUSED JUNCTION p⁺n InP SOLAR CELLS FOR SPACE APPLICATIONS

Mircea Faur
Cleveland State University
Cleveland, Ohio

C. Goradia
Cleveland State University
Cleveland, Ohio

Maria Faur
NYMA, Inc.
Brook Park, Ohio

N.S. Fatemi and P.P. Jenkins
NYMA, Inc.
Brook Park, Ohio

D.J. Flood and D.J. Brinker
NASA Lewis Research Center
Cleveland, Ohio

D.M. Wilt and S. Bailey
NASA Lewis Research Center
Cleveland, Ohio

M. Goradia and J. Moulot
Cleveland State University
Cleveland, Ohio

ABSTRACT

Recently, we have succeeded in fabricating diffused junction p⁺n(Cd,S) InP solar cells with measured AM0, 25 °C open circuit voltage (V_{OC}) of 887.6 mV, which, to the best of our knowledge, is higher than previously reported V_{OC} values for any InP homojunction solar cells. The experiment-based projected achievable efficiency of these cells using LEC grown substrates is 21.3%. The maximum AM0, 25 °C efficiency recorded to date on bare cells is, however, only 13.2%. This is because of large external and internal losses due to non-optimized front grid design, antireflection (AR) coating and emitter thickness. This paper summarizes recent advances in the technology of fabrication of p⁺n InP diffused structures and solar cells, resulted from a study undertaken in an effort to increase the cell efficiency. The topics discussed in this paper include advances in: 1) the formation of thin p⁺ InP:Cd emitter layers, 2) electroplated front contacts, 3) surface passivation and 4) the design of a new native oxide/Al₂O₃/MgF₂ three layer AR coating using a chemically-grown P-rich passivating oxide as a first layer. Based on the high radiation resistance and the excellent post-irradiation annealing and recovery demonstrated in the early tests done to date, as well as the projected high efficiency and low-cost high-volume fabricability, these cells show a very good potential for space photovoltaic applications.

INTRODUCTION

Owing to their excellent radiation resistance and annealing properties (refs. 1, 2), InP solar cells hold great promise for space power applications. In 1990, within a few short years after the renewed interest in the development of InP solar cells began in 1985, driven by early reports from NTT, Japan (ref. 4), an AM0, 25 °C efficiency of 19.1% was already achieved on a 4 cm² InP cell (ref.5). These n⁺pp⁺(Si,Zn) InP cells, developed by SPIRE Corp., were fabricated by MOCVD growth of the active layers on a heavily doped p⁺-InP:Zn substrate. The achievement of such a high efficiency in such a short period of time is particularly important since no special efforts were made to reduce external losses associated with an unpassivated surface and with the use of a ZnS/MgF₂ AR coating, developed for GaAs based solar cells. An unpassivated surface is suggested both by the low V_{OC} value of 876 mV, and the low blue response for an emitter thickness of only 30 nm. By passivating the front surface, the projected AM0, 25°C efficiency of 22% for these cells seems very realistic. Given this unprecedented short term success in developing high efficiency InP solar cells, and the relatively large accepted potential of these cells for high radiation environment space solar cells applications, it is rather odd that research funds from the space agency have continuously declined after 1990. A possible explanation of this, besides shrinking research funds, is the high cost of presently developed all-epitaxial high efficiency InP solar cells. For small power applications, where, beside radiation resistance, high BOL efficiency is required, the use of all-epitaxial InP solar cells grown on

InP substrates might be justified. However, their high wafer and processing costs, prohibit their large scale use in space solar cell arrays.

The cost of InP cells is due, to a significant extent, to the high cost of InP substrates. Hence, a large cost reduction might be achieved through heteroepitaxial InP solar cells grown on cheaper substrates such as Si or Ge. The increase in their AM0, 25 °C efficiency above presently achieved 7.1% (ref.6) for Si and 9% (ref. 7) for Ge substrates respectively is expected to come through the growth of GaAs based intermediate layers to accommodate the large lattice mismatch between InP and Si or Ge. Should these heteroepitaxial cells exhibit a BOL efficiency in excess of that of presently used Si space solar cells while retaining the radiation tolerance of homojunction InP solar cells, then, due to their lighter weight, lower substrate cost, and lower fragility, as compared to all-InP solar cells, they would have a very good potential for large scale use in space solar arrays, provided that the processing costs could be kept within reasonable limits.

A significant cost reduction over epitaxy can be achieved through the use of diffused junction InP cells. Until recently, the only InP solar cells fabricated by thermal diffusion were of the n^+p configuration. Cells fabricated by closed ampoule diffusion have yielded maximum AM0, 25 °C efficiency of 16.6% for a (S,Zn) cell (ref.8), 14.35% for non-optimized (S,Cd) cell (ref.9), and 15.2% for an open tube diffusion (S,Zn) cell (ref.10). The n^+p (S,Zn) InP cells made by closed ampoule diffusion have high radiation resistance (ref.1), and independent studies (e.g. refs. 11, 12) have shown much higher annealing rates after irradiation, under cell operating conditions, than high efficiency $n^+/n^+/p/p^+$ (Si,Zn) all-MOCVD InP cells (ref.5).

The drawback of the n^+p (S,Zn) diffused InP cells is that a large number of defects are present after diffusion both in the n^+ emitter and in the p-base, which, as shown above, makes the solar cell efficiency lower than that of all-MOCVD n^+p (Si,Zn) InP cells. Since, neglecting surface effects, of all solar cell performance parameters, V_{OC} can be regarded as the best measure of how low is the defect density within a given cell structure from among the different cell structures, its value can give useful information about the quality of each cell structure. For example, for the best n^+p (S,Zn) diffused cell with AM0, 25 °C efficiency of 16.6%, measured at NASA LeRC, the V_{OC} was only 828 mV as compared to 876 mV for the higher AM0 efficiency (19.1%) of the MOCVD-grown cell.

At the 11th SPRAT Conference, we predicted that for diffused solar cells, the p^+n configuration has a higher potentially achievable maximum efficiency than the n^+p configuration due especially to an increased V_{OC} (ref.13). The prediction was based on AM0, 25 °C V_{OC} values of 860 mV we measured for p^+n (Cd,S) InP solar cells as compared to experiment-based projected maximum V_{OC} of only 840 mV for our n^+p (S,Cd) InP cells. For our thermally diffused p^+n and n^+p structures, the ranking for projected maximum efficiency, in decreasing order, is: (1) p^+n (Cd,S); (2) n^+p (S,Cd); (3) n^+p (S,Zn), and (4) p^+n (Zn,S). The large structural and electrical-type defect density we found in the emitter and the base of structures (2) to (4) as compared to structure (1), explains V_{OC} , I_{SC} , and η limitations of the last three structures. This also explains why, although a large experimental effort was made by NTT to improve V_{OC} and efficiency of diffused n^+p (S,Zn) cells, the independently confirmed maximum efficiency was of only 16.6%. However, more recent work performed on NTT fabricated n^+p cells (ref.14) has shown that the AM0 efficiency of one such cell could be increased from 14.8% to 17.5% by plasma hydrogenation at 150 °C. The large gain in η is due to a sensitive increase in J_{SC} , which is thought to be due to a decrease in H2 and H3 trap center densities in the p-InP:Zn base, and the formation of a n^+-p-p^+ structure. A small increase in V_{OC} is thought to be due to a decrease by hydrogenation in surface and space charge recombination. For n^+p structures, we found Cd-doped substrates to be inherently superior to Zn-doped substrates (ref.10), and the experiment based practically achievable AM0 efficiency of diffused n^+p (S,Cd) InP solar cell using relatively large EPD ($\sim 5 \times 10^4 \text{ cm}^{-2}$) substrates is about 18.8%.

A preliminary investigation of p^+n and n^+p diffused structures and solar cells, prior to and after irradiation with 10^{13} cm^{-2} 3 MeV protons indicates that the same ranking should hold for structures (1), (2), and (4) with respect to radiation resistance as mentioned above for maximum efficiency. The p^+ emitter of p^+n (Cd,S) InP diffused structures exhibits very low radiation induced carrier removal rates (ref.16), which is thought to contribute to the increased radiation resistance of these cells as compared to other InP cell structures for which 3 MeV proton irradiation studies are available. Another interesting characteristic of

these cells is a remarkable annealing property at room temperature in the dark, which might be very attractive for other applications such as long-life alpha- or beta-voltaic batteries.

Recently, using a P-rich passivating layer grown by chemical oxidation, we have succeeded in fabricating diffused junction $p^+n(\text{Cd,S})$ InP solar cells with measured AM0, 25 °C V_{OC} of 887.6 mV (ref.16), which to the best of our knowledge is higher than previously reported V_{OC} values for any InP homojunction solar cells. Although the experiment based projected achievable efficiency of these cells using LEC grown substrates is 21.3% (ref.17), the maximum AM0, 25 °C efficiency recorded to date on bare cells is only 13.2%. This is because of large external and internal losses due to non-optimized front grid design, antireflection coating (ARC) and emitter thickness. This paper summarizes recent advances in the technology of fabrication of p^+n InP diffused structures and solar cells, resulting from a study undertaken in an effort to increase the cell efficiency. These advances include: 1) the formation of thin p^+ InP:Cd emitter layers, 2) electroplated front contacts, 3) surface passivation and 4) the design of a new native oxide/ $\text{Al}_2\text{O}_3/\text{MgF}_2$ three layer AR coating using a chemically-grown P-rich passivating oxide as a first layer. The paper will also discuss some light instability problems associated with high Zn content front Au-Zn contacts and preliminary radiation resistance and post-irradiation annealing studies.

EXPERIMENTAL

Cd diffusion into $n\text{-InP:S}$ ($N_D - N_A = 3.5 \times 10^{16}$ to $3.1 \times 10^{17} \text{ cm}^{-3}$) was performed by a closed ampoule technique using Cd_3P_2 as diffusion source (ref.18). Diffusion temperatures were from 560 to 660 °C. The substrates were Czochralski (LEC) grown with EPD of about $5 \times 10^4 \text{ cm}^{-2}$. Diffusions were performed through either P-rich chemically grown (ref.13) or MOVPE grown InGaAs cap layers.

The surface quality of diffused samples was monitored by either Nomarski or SEM microscopy. Electrochemical techniques (ref.19) were used for step-by-step characterization of these diffused structures during fabrication and after irradiation with high energy protons using a Polaron profiler PN4200, manufactured by BIORAD. We have recently developed a new electrolyte, which we call "UNIEL", for EC-V profiling of InP and GaAs based structures (ref. 19). In order to accurately locate the position of different defect levels derived from low frequency EG-V measurements, we have began, in parallel, photoluminescence measurements at 5 K on several Cd diffused samples. The excitation wavelength was 514 nm at a power density of 160 mW/cm^2 . Luminescence was dispersed in a 1.26 meter spectrometer and detected with cooled CCD array. The system resolution was about 0.5 meV.

Small area (0.48 cm^2) p^+n InP solar cells were fabricated using Zn- and Cd-diffused structures. Au was used for the back contact. The Au-Zn-Au (0.18 to $1.5 \mu\text{m}$ thick) front contact grid was deposited by evaporation and defined using existing photolithographical masks, designed for n/p cell configurations. Au based contacts are known to penetrate into InP during sintering at 430 °C up to depths which are over three times the initial thickness of the evaporated Au-Zn-Au layer. Hence, we kept the thickness of the emitter at quite a high value (up to $5 \mu\text{m}$) while keeping the thickness of the evaporated contacts below $0.2 \mu\text{m}$. After sintering, the thick emitter was thinned down over the uncontacted area using a chemical etch (PNP), specially developed for this purpose (ref.20). Recently we were able to fabricate thin p^+ emitters using Cd-diffusion, by using either thicker P-rich oxides or InGaAs cap layers. New front contact schemes, employing electroplated Au and Au-Zn developed for thin emitters will be discussed in the following paragraph. We also propose a new optimized three-layer ARC for InP solar cells, which uses a P-rich chemical oxide as a first layer in a $\text{In}(\text{PO}_3)_3/\text{Al}_2\text{O}_3/\text{MgF}_2$ structure. This P-rich chemical oxide, which is described in more detail elsewhere (ref.16), is primarily designed as a surface passivation layer.

Unless otherwise mentioned, the performances of solar cells in this paper refer to non optimized single layer ARC using only the passivating layer. Dark and illuminated solar cell performances and their variation with illumination time or temperature were recorded at CSU using a computer controlled facility and an ELH lamp (assumed AM1.5 spectrum) as the light source. For selected cells, dark and illuminated I-V characteristics, and their variation with time, as well as reflectivity and spectral response measurements were performed at NASA LeRC.

RESULTS AND DISCUSSION

At the last SPRAT conference we reported an AM0, 25 °C, V_{OC} value of 880.3 mV for a diffused p^+n (Cd,S) InP solar cell. Since the maximum efficiency was only 12.57% as compared to projected achievable maximum efficiency of 21.3%, over the last year we have concentrated our efforts to reduce the large external and internal losses due to non optimized front grid contacts, AR coatings and emitter thickness, while further improving the diffused structure quality, by reducing the defect density in the emitter and junction area.

Since, of all solar cell parameters, V_{OC} can be regarded as the best measure of how low is the defect density within a given structure from among the different cell structures, its value can give useful information about the quality of each cell structure. Recently, using a P-rich passivating layer grown by chemical oxidation, we have succeeded in fabricating diffused junction p^+n (Cd,S) InP solar cells with measured AM0, 25 °C V_{OC} of 887.6 mV (Fig.1), which to the best of our knowledge is higher than previously reported V_{OC} values for any InP homojunction solar cells. The achievement of such a high V_{OC} value for a diffused junction cell with no AR coating, except for the thin passivating layer, is remarkable if one takes into consideration that the InP:S LEC grown substrates used have had a rather large EPD of $5-7 \times 10^4 \text{ cm}^{-2}$. From the dark I-V characteristic (Fig.2), the dark saturation current density J_0 ($A=1$) has a record low value of $1.38 \times 10^{-17} \text{ A/cm}^2$, which explains the high V_{OC} value.

The cell was fabricated by thinning the emitter from its initial thickness of about 4.5 μm to about 0.45 μm , after sintering the Au-Zn front contact. The relatively low short circuit current density (J_{SC}) of 26.3 mA/cm^2 and the low external quantum efficiency (EQY) of this cell can be explained by the large thickness of the emitter (0.45 μm , compared to the optimum thickness of $\sim 0.25 \mu\text{m}$) and the absence of an AR coating. Figure 3 shows the EQY of this cell. Worth noticing is the relatively high blue response for a p^+ emitter as thick as 0.45 μm , suggesting a large diffusion length in the Cd doped emitter and a well passivated surface. The cell had a high R_s of about 3.5 $\Omega\text{-cm}^2$ due to relatively high contact and sheet resistance and non optimized front grid design (an existing photolithographical mask designed for n/p cell configurations was used), resulting in low FF of 69% and efficiency of only 11.98%.

Next paragraphs summarize recent advances in p^+n InP diffused structures and solar cell technology, undertaken in an effort to increase the cell efficiency. This includes the formation of thin p^+ -InP:Cd emitter layers, electroplated front contacts, surface passivation and the design of a new native oxide/ Al_2O_3 / MgF_2 three layer AR coating structure using a chemically-grown P-rich passivating oxide as a first layer. Also discussed are some light instability problems associated with high Zn content front Au-Zn contacts and preliminary radiation resistance and post-irradiation annealing studies.

Emitter Layer

As mentioned above, for cells such as that shown in Fig.1, thick emitters have been used. This adds a troublesome fabrication step, which affects the reproducibility of cell performances. Furthermore, as seen above, using thick emitters such as in Fig.4, thinning from over 4 μm to below 0.5 μm has the drawback of reducing the surface hole concentration in the thinned emitter, thereby increasing the series resistance (R_s) and lowering the fill factor (FF). A more step-like diffusion profile such as in Fig.5, was possible by optimizing the thickness of the $\text{In}(\text{PO}_3)_3$ -rich chemical oxide ($\sim 10 \text{ nm}$), used as a diffusion cap layer. To further decrease the R_s values of these cells, two avenues were undertaken:

- Since the optimal emitter thickness is estimated at about 0.25 to 0.3 μm , we were able to fabricate thin emitters while maintaining the high surface acceptor concentration (see Fig.6).
- Use low band gap diffusion cap layers such as InGaAs. Example: The EC-V diffusion profile in Fig.7(a) was realized using an intentionally undoped InGaAs cap layer. Curve (b) refers to a diffusion carried out under similar conditions (600 °C, 25 min., and same amount of Cd_3P_2 source material) using a thin $\text{In}(\text{PO}_3)_3$ -rich chemical oxide cap layer. As expected, the InGaAs cap, after Cd diffusion becomes highly doped, which should improve the contact

resistance. However, in this case, since InGaAs cap is not stable at higher temperatures, the hole concentration in the InP:Cd emitter is rather low, which should increase the sheet resistance.

Electroplated Front Contacts.

For thin emitters (0.5 to 0.75 μm) we first tried thin (0.1 μm) Au-Zn evaporated contacts, with an intent to then deposit thicker electroplated contacts after sintering. However, after sintering the contacts at 430 $^{\circ}\text{C}$, for 2 minutes, the contacts penetrated at depths greater than the emitter thickness, short-circuiting it. For lower sintering temperatures the contacts lifted during subsequent chemical treatments in PNP etch (ref.20) we are using both for surface passivation and thinning the emitter. For these samples, after removing the evaporated contacts, Au-Zn and Au-Cd front contacts were fabricated using conventional UV lithography and electroplating. The positive photoresist ($\sim 5 \mu\text{m}$ thick) was deposited on clean and chemically oxidized emitter surfaces. In both cases about 0.5 μm Au-Zn or Au-Cd were first electrodeposited by pulse plating at pulse current density of 0.5 to 2 mA/cm^2 , then 5 to 18 μm Au was deposited at a constant current density of 0.2 to 0.3 mA/cm^2 . When using clean surfaces the width of the contact grid fingers became up to 3 times the designed values, while their width have not increased significantly when a 20 to 50 nm chemical oxide was used. Electroplated Au-Zn or Au-Cd front contacts we found are well suited for deposition on thin emitters since they do not require sintering. For example, using $\sim 8 \mu\text{m}$ thick electroplated Au-Zn contacts, grown on a 0.6 μm thick emitter, using an oxidized surface, we recorded R_s values as low as 1.28 $\Omega\text{-cm}^2$, and FF values of over 80%, after thinning the emitter to about 0.3 to 0.4 μm . Since for p/n configuration the sheet resistance is a major contributor to R_s , we estimate that by using an optimized front grid mask, R_s values of less than 0.5 $\Omega\text{-cm}^2$ and FF greater than 84% can be achieved after thinning the p⁺ emitter such as in Fig.6 to 0.25-0.3 μm .

Surface Passivation

One of the key factors limiting the performance of InP solar cells is their high surface recombination velocity (SRV), which is estimated, even for epitaxially grown cells to be as high as 10^7 cm/s (ref.21). Although not near to such an extent as the n⁺p InP structures, p⁺n InP structures fabricated by thermal diffusion have their surface stoichiometry destroyed. Therefore, it is important in the fabrication of high-performance InP solar cells in general and diffused InP cells in particular, to remove in a controlled manner the high defect density surface layer of the emitter and to passivate the surface. Calculations have shown that SRVs higher than $5 \times 10^5 \text{ cm/s}$ drastically reduce the efficiency of InP solar cells by lowering their blue response (ref.22). Simple chemical treatments of InP surfaces using HNO₃ and HF based etchants (ref.23) were found to decrease the SRV to below $5 \times 10^5 \text{ cm/s}$, e.g. 1.7×10^5 for n⁺-InP and $4.7 \times 10^5 \text{ cm/s}$ for p⁺-InP, after rinsing the substrates in a HNO₃ (15%) solution (ref.24).

Using the PNP etch, based on HNO₃, o-H₃PO₄, and H₂O₂, we developed for thinning after contacting the p⁺-InP emitter (ref.20), from low frequency EG-V measurements, we recorded a surface state density minimum (N_{ss}) at the Cd-diffused p⁺-InP/passivating layer interface as low as $2 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$. About 40 nm was removed from the surface of a the p⁺n InP structure diffused at 660 $^{\circ}\text{C}$ (surface acceptor concentration: $\sim 4 \times 10^{18} \text{ cm}^{-3}$). Such a low N_{ss} value is in good qualitative agreement with the high measured V_{oc} and blue response values of solar cells fabricated on these structures.

AR Coating

The residual oxide grown on p⁺-InP using the PNP etch is composed of a thick In-rich outer layer and a P-rich layer at the interface with the emitter (Fig.8). From XPS investigation (ref.20), the interfacial oxide is rich in In(PO₃)₃. Since this oxide, as seen above, passivates the surface quite well, and it has a bandgap of $6.8 \pm 0.2 \text{ eV}$ (ref. 25), we proposed that it be used as a first layer AR coating (ref.16). The transparency of

this oxide over the measured 1.8 to 5.2 eV range (ref.25) and its low blue reflectivity, as compared to SiO, Sb₂O₃, shown in Fig.9, and optimized ZnS/MgF₂ double layer AR coating (not shown here), seem to make this oxide a very attractive candidate, indeed, for use as a first layer AR coating. In addition, when we deposited on our bare p⁺n InP cells either SiO or Sb₂O₃ or a double layer of ZnS/MgF₂, the V_{OC} dropped by as much as 50 mV, indicating a large increase in SRV. As shown in Fig.10, the two layered oxide (~ 130 nm) reduces the reflectance of an p⁺n InP solar cell from an average of 40% to slightly less than 20%. In this particular case, after removing the In-rich outer-oxide layer, the reflectance of the remaining thin In(PO₃)₃ oxide is about 25%.

Although the overall reflectance of the double-layered chemical oxide in Fig.9 is lower than that of SiO, it is still too high for use as a single layer AR coating. Furthermore, the outer In-rich oxide is unstable and quite conductive, which caused for our cells a noticeable drop in R_{SH}, and V_{OC}. Therefore, we removed it, and in our best design we add Al₂O₃ and MgF₂ as second and third layers of the three-layer coating. For the example in Fig.10, a three-layer AR coating composed of In(PO₃)₃ (45 nm) / Al₂O₃ (62 nm) / MgF₂ (41 nm), reduces the overall reflectivity (no grid fingers) to less than 2%. Details of this design will be given elsewhere (ref.26).

Progress in p⁺n InP Diffused Solar Cells

As mentioned above, our efforts over the last year or so were concentrated on designing: 1) thin p⁺-InP emitters, 2) front contacts, 3) passivating layer and 4) AR coating, so as to minimize the large external losses present in our cells. Therefore, since these efforts were made simultaneously, solar cells were only fabricated to check our progress and to correlate other measured parameters to solar cell parameters. Table 1 shows some preliminary results. As an example, by using a more step-like diffusion profile of Fig.5 for cell #3, instead of the more graded profile of Fig.4 for cell #1, the R_S value could be noticeably decreased, using the same n-type front grid design. An increased FF made it possible to increase the AM0 efficiency from 11.25% to 13.2%. The relatively lower V_{OC} for cell #3 is due to current leakage which occurs through the In-rich oxide (~ 110 nm) outside the mesa etched active area. This is confirmed by the data of cell # 4. As seen, upon removing the In-rich outer layer, although the J_{SC} value decreased, as expected from the reflectivity measurements such as shown in Fig.10, the V_{OC} value increased. The small increase in FF was due to an increase in R_{SH}. By depositing a non-optimized SiO (~ 85 nm) second AR coating layer, the cell current density increased by about 12%. To make sure that no current is collected from outside the active area of the cell, this particular cell was cleaved around the mesa etched defined lines, and no noticeable changes in cell AM0 parameters were observed.

From correlations between measured cell parameters, reflectivity, spectral response, dark saturation current densities and J_{SC}-V_{OC} plots, the projected AM0, 25 °C performance parameters of p⁺n (Cd,S) InP solar cells, using our state-of-the-art newly developed thin emitters, and optimal front grid (6% coverage), and the newly designed three layer AR coating, are: V_{OC}=910 mV, J_{SC}=37.85 mA/cm², FF=84%, and η =21.2%. These performances are predicted for an emitter thickness of 0.3 μm, a surface acceptor concentration of 3.5x10¹⁸ cm⁻³, base electron concentration of 7.5x10¹⁶ cm⁻³, front SRV of 10⁵ cm/s, and using LEC grown InP:S substrates with EPD=5x10⁴ cm⁻². Higher efficiency is possible by using better quality substrates, further improving the diffused structures and the cell fabrication sequences.

Some light degradation effects have been observed in our earlier p⁺n (Cd,S) cells, which we have attributed to excess Zn content (> 10%) in the Au-Zn front contacts. Indeed, as seen in Fig.11 by lowering the Zn content to less than 10%, the relative degradation of cell parameters decreases from about 10% to less than 1%. We believe that by using lower Zn content (0.1 to 1%) Au-Zn front contacts, which recent studies indicate to offer a lower contact resistance, this problem can be eliminated. We observed similar degradation effects in our n⁺p (S,Zn) diffused cells with high base acceptor concentration (> 10¹⁷ cm⁻³). However, as seen in Fig.11 no light degradation is observed for a cell with lightly base doping (2.4 x 10¹⁶ cm⁻³).

Preliminary Radiation Resistance and Annealing Studies.

Preliminary results of radiation resistance studies of diffused p^+n (Cd,S) InP solar cells, such as shown in Table 2, indicate that the percent of remaining power (39%), after irradiation with 10^{13} cm^{-2} , 3 MeV protons is higher than that of other InP cell structures, including the all-MOCVD fabricated n^+p (Si,Zn) and diffused n^+p (S,Zn) InP cells, for which irradiation data using 3 MeV protons are available (ref.15). Furthermore, this cell shows a remarkable annealing property at room temperature (RT) in the dark. The AM0, 25 °C, performance parameters of this cell prior to irradiation and after about 1 year at RT in the dark, are shown in Table 3. Subsequent light soaking of this cell for 1 hour under AM1.5, 25 °C, raised its efficiency by about 2.5% (See Fig.11), indicating good annealing properties under illumination.

Preliminary radiation resistance studies and annealing studies of these cells have been started at Spire Corp., after irradiation with high energy alpha particles. For one such cell, for which data are available, after irradiation at an equivalent 1MeV e^- fluence of $1.06 \times 10^{17} \text{ e}^-/\text{cm}^2$, which corresponds to over 100 years in GEO, the remaining power output is 32% of the initial power (Table 4). As a result of a significant recovery of about 6%, after only 4 days at RT in the dark, and an expected higher recovery rate under the cell operating conditions (RT, under illumination), these cells are not expected to degrade significantly in high radiation environment orbits, even after such large fluences.

We attribute the high radiation resistance of diffused p^+n (Cd,S) InP cells to a very low carrier removal rate (Fig.12) in the emitter (ref.15). It is note worthy that the carrier removal in the InP:S base, after irradiation with 10^{13} cm^{-2} , 3 MeV protons has decreased by more than an order of magnitude. For a thick p^+ emitter, most of the cell current is not expected to come from the base or space charge region. Since, as seen, the more heavily doped Cd-diffused emitter degrades less than the low doped base, the superior radiation resistance of these cells, as compared to a thin emitter n^+p configuration with a thin emitter, should be expected.

Low Cost Processing Scheme for High Efficiency Radiation Resistant p^+n InP Diffused Solar Cells.

For InP solar cells to be commercially useful for practical space mission applications, their cost must be significantly reduced, and they should achieve high BOL and EOL efficiencies. For small to medium power requirements, the weight might not be a prime requirement, as long as the cells are intended for high radiation environments. Diffused structures InP cells in general, and p^+n (Cd,S) cell structures in particular, appear to be more radiation resistant than cells fabricated by epitaxy. A simplified processing scheme is proposed in Fig.13, for fabrication of high efficiency, radiation resistant p^+n InP diffused junction cell. The scheme we propose ensures not only a low fabrication cost, but also high throughput and reproducibility.

As shown in the previous paragraphs, preliminary results show that cells using Cd-diffused emitter have not only a good potential for achieving high BOL efficiencies, but they also appear to be more radiation resistant and to have better post irradiation annealing properties than other diffused cell structures. Since for the p^+n configuration, the Cd-diffused cells are more radiation resistant than the Zn-diffused emitter cells fabricated using similar S-doped substrates, it will be very interesting to see how the radiation resistance of epitaxial and diffused n^+p cells, with similar structures, e.g. (S,Zn) do compare. Also it would be interesting to compare p^+n InP homojunction or heteroepitaxial cell structures with the emitter diffused into a thin base grown epitaxially on heavily doped InP or cheaper substrates such as GaAs, Ge or Si with all-epitaxial grown similar cell structures.

CONCLUSIONS

- We have found the ranking in decreasing order of projected maximum efficiency of diffused junction InP solar cells to be: 1) p^+n (Cd,S), 2) n^+p (S,Cd), 3) n^+p (S,Zn), and 4) p^+n (Zn,S). Preliminary investigation indicates the same ranking holds for these structures with respect to radiation resistance.

- If further developed, the p⁺n (Cd,S) InP solar cells, developed by CSU/NASA LeRC, offer the following significant advantages for space power applications:
 - Low processing cost
 - High throughput
 - Good reproducibility
 - High projected efficiency
 - High radiation resistance
 - Self annealing during operation
- The radiation resistance of these cells, combined with their annealing behavior under operating conditions, may eliminate the need for shunt circuits used in conventional satellites to dump excess power early in their missions.
- Although InP has about twice the density of Si, or Ge substrates, the ability of diffused InP to anneal under operating conditions allows the thickness of the protective cover glass to be reduced, compensating for the difference in the substrate weight.
- The technology of InP diffused structures, electroplated contacts, In(PO₃)₃/Al₂O₃/MgF₂ ARC, and improved electrochemical characterization techniques, developed in this work, can be applied to fabrication of other III-V solar cell and opto-electronic devices.

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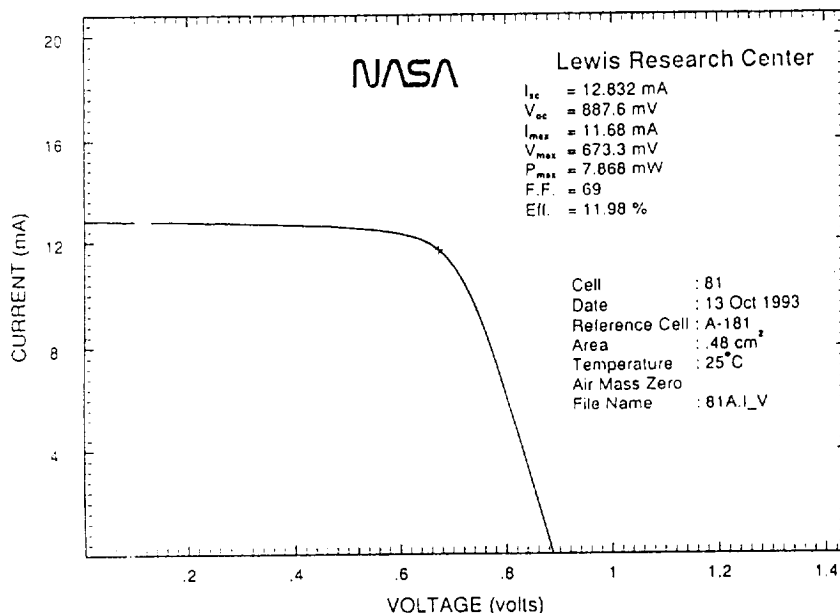


Fig.1. AM0, 25 °C illuminated I-V characteristic. Emitter thickness: ~ 0.45 μm ; AR coating: ~ 30 nm $\text{In}(\text{PO}_3)_3$.

Table 1: AM0, 25°C performances of selected diffused junction p⁺n (Cd,S) InP solar cells measured at NASA LeRC

Cell #	Diffusion Profile such as in:	AR coating	Approx. emitter thickness (μm)	Rs (Ω-cm ²)	Jsc (mA/cm ²)	Voc (mV)	FF (%)	η (%)
1	fig. 4	In(PO ₃) ₃ ^b (~300Å)	0.35	4.92	27.6	886.9	62.8	11.25
2	fig. 5	In(PO ₃) ₃ ^b (~400Å)	0.45	3.24	27.5	884.6	73.7	12.95
3	fig. 5	In ₂ O ₃ ^a (900Å)/ In(PO ₃) ₃ ^b (~300Å)	0.4	3.35	28.2	881.7	72.6	13.2
4	fig. 4	In ₂ O ₃ ^a (1100Å)/ In(PO ₃) ₃ ^b (~400Å)	0.3	4.38	29.4	877.2	61.7	11.63
		In(PO ₃) ₃ ^b (~400Å)			27.6	886.6	62.8	11.25
		SiO (~850Å)/ In(PO ₃) ₃ ^b (~400Å)			30.95	887.3	61.5	12.36

The residual chemical oxide after dissolving the p⁺ InP emitter using the PNP etch [4], has two components: (a) a thick In₂O₃-rich surface layer, and (b) an interfacial In(PO₃)₃-rich layer.

Table 2: AM1.5, 25°C performance parameters of a diffused p⁺n (Cd,S) InP solar cell before (b) and after irradiation with 10¹³ cm⁻², 3MeV protons.

Time after irradiation (hours)	Voc (mV)	Jsc (mA/cm ²)	FF (%)	η (%)	Rs (Ω-cm ²)
0 (b)	871	27.42	72.64	12.65	3.27
8	664	15.48	64.00	4.86	5.33
90	676	16.37	65.10	5.25	5.19
206	682	16.85	65.50	5.49	4.88
857	708	18.47	66.00	6.29	4.85

(*) The cell was kept at RT in the dark except for 6 short exposures to light during illuminated I-V measurements

Table 3: AM0, 25°C performance parameters of a p⁺n (Cd,S) InP solar cell (same as in Table 2), before (b) irradiation and 1 year after irradiation (a) with 10¹³ cm⁻² 3MeV protons.

	Voc (mV)	Jsc (mA/cm ²)	FF (%)	η (%)
(b)	880.3	26.81	73.1	12.57
(a)	713.9	18.02	67.0	6.31

(*) Measurements performed at NASA LeRC. After irradiation, the cell was kept at RT in the dark except for 6 light exposures during the AM1.5, 25°C illuminated I-V measurements in Table 2.

Table 4: AM0, 25°C performance parameters of a CSU p⁺n (Cd,S) InP solar cell prior to and after alpha irradiation at 1MeV equivalent electron fluence of 1.06x10¹⁷ cm⁻². (*)

	Voc (mV)	Jsc (mA/cm ²)	FF (%)	η (%)	J ₀₁ (n ₁ =1) (A/cm ²)	J ₀₂ (n ₂ =2) (A/cm ²)	R _s (Ω-cm ²)	R _{sh} (x 10 ⁵ Ω)
Before irradiation	888	27.18	69.21	12.17	2.85 10 ⁻¹⁷	7.7 10 ⁻¹¹	3.66	5.1
Post irradiation	652	13.64	60.14	3.90	2.72 10 ⁻¹⁴	3.4 10 ⁻⁰⁸	6.04	2.8
After 4 days at RT in the dark	659	14.32	60.14	4.13	2.1 10 ⁻¹⁴	3.05 10 ⁻⁰⁸	5.91	2.6

(*) The measurements and irradiation were performed at SPIRE Corp., and presented here with permission from Dr. C. Blatchley.

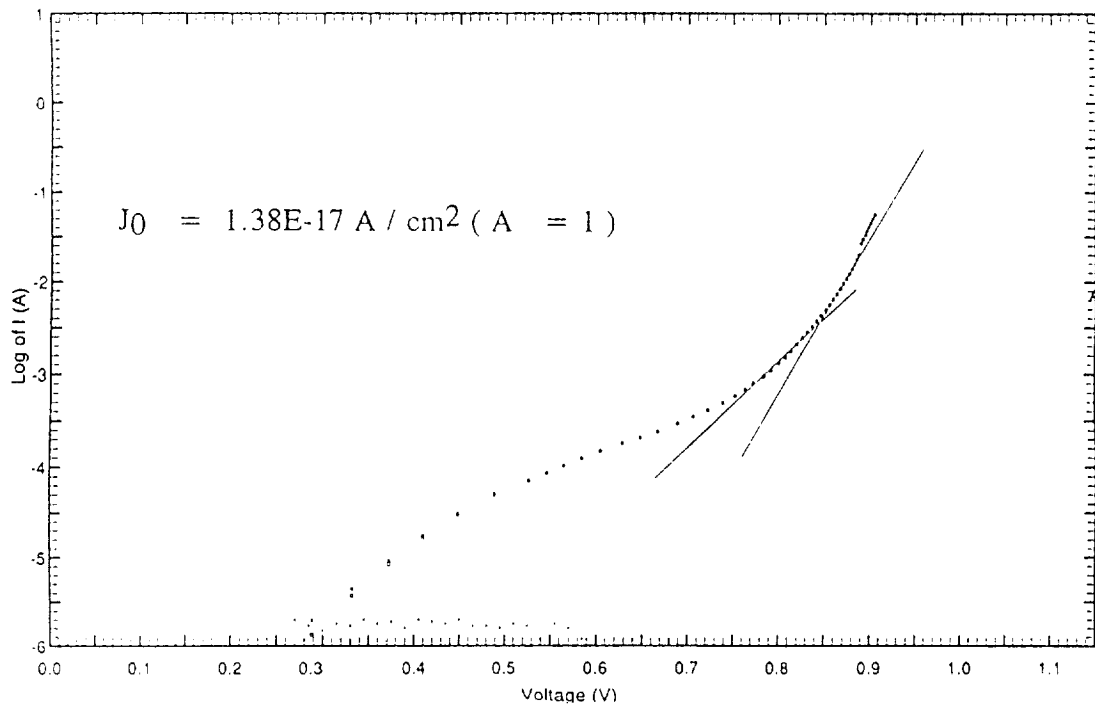


Fig. 2. Dark I-V characteristic of cell # 4 in Table 1.

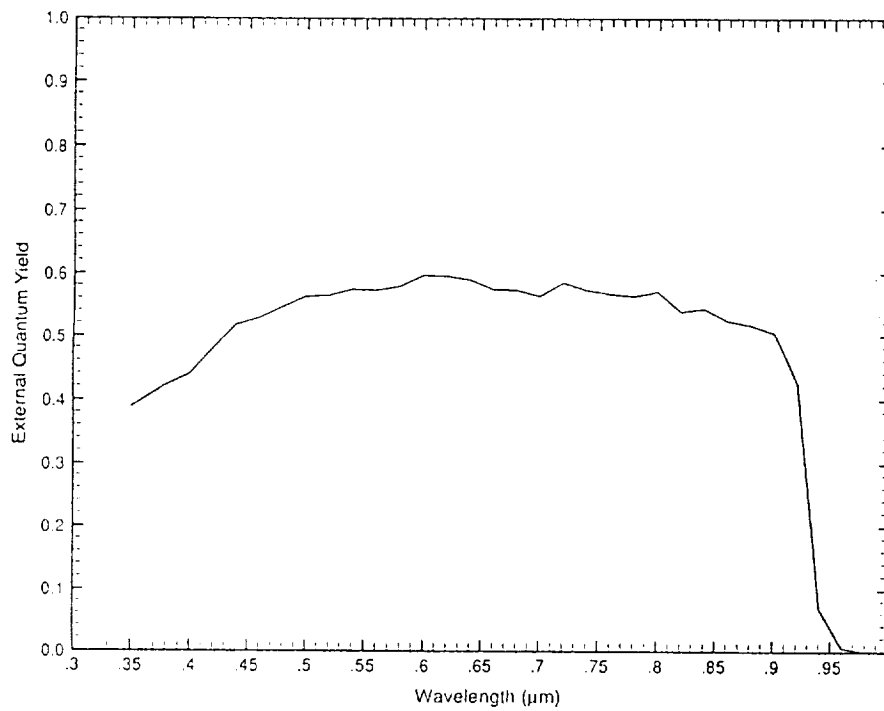


Fig. 3. Typical EQY plot of a cell with a thin $\text{In}(\text{PO}_3)_3$ (~ 30 nm) as an AR coating. Overall reflectivity: ~ 30%. Emitter thickness: ~ 0.45 μm .

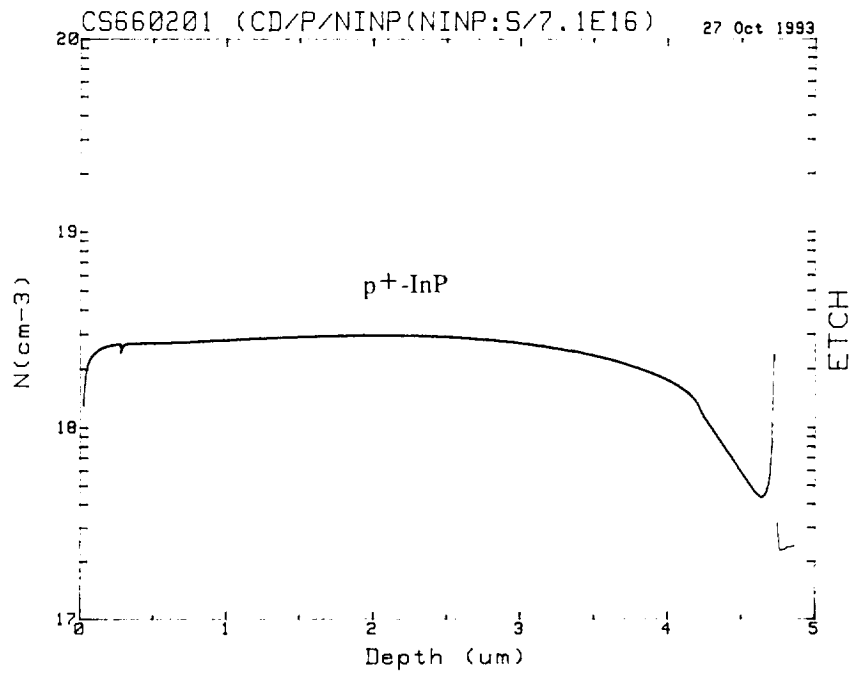


Fig.4. EC-V profile of a p⁺n (Cd,S) InP structure diffused at 660 °C. Diffusion cap: In(PO₃)₃ (~ 3 nm).

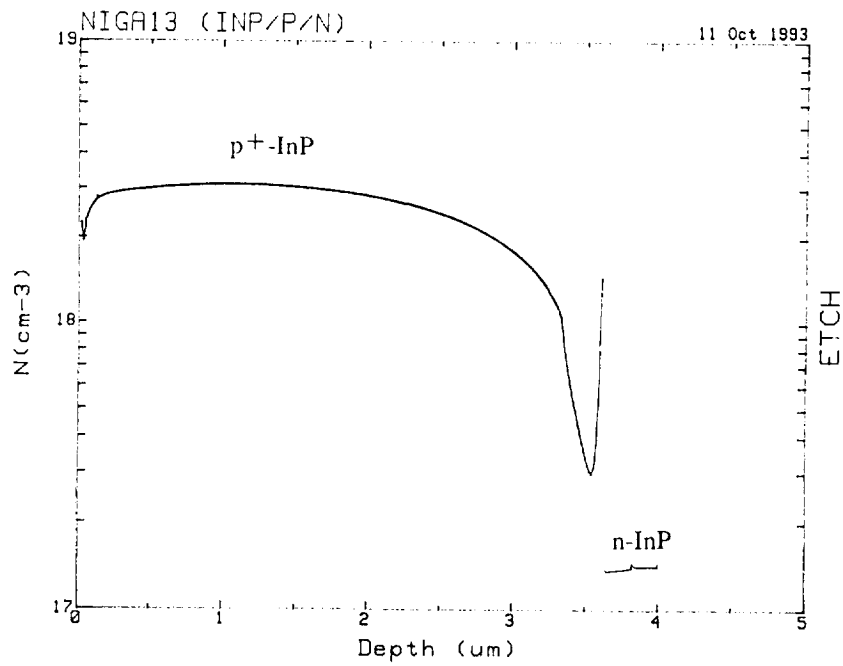


Fig.5. EC-V profile under similar conditions as in Fig. 4, but using ~ 10 nm thick In(PO₃)₃ diffusion cap.

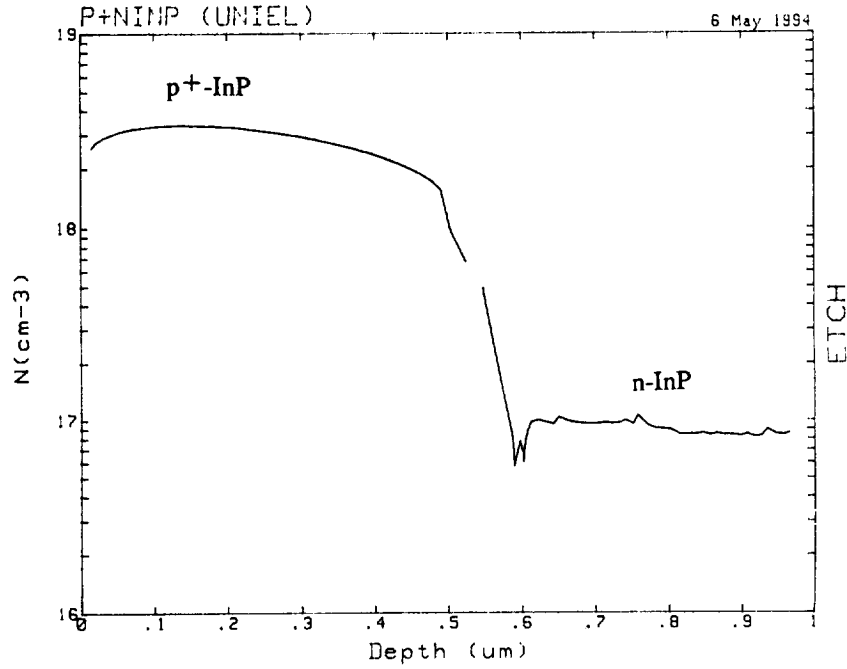


Fig.6. Thin emitter p^+n (Cd,S) InP EC-V profile, at 660 °C. using $\text{In}(\text{PO}_3)_3$ (~ 3 nm thick) diffusion cap.

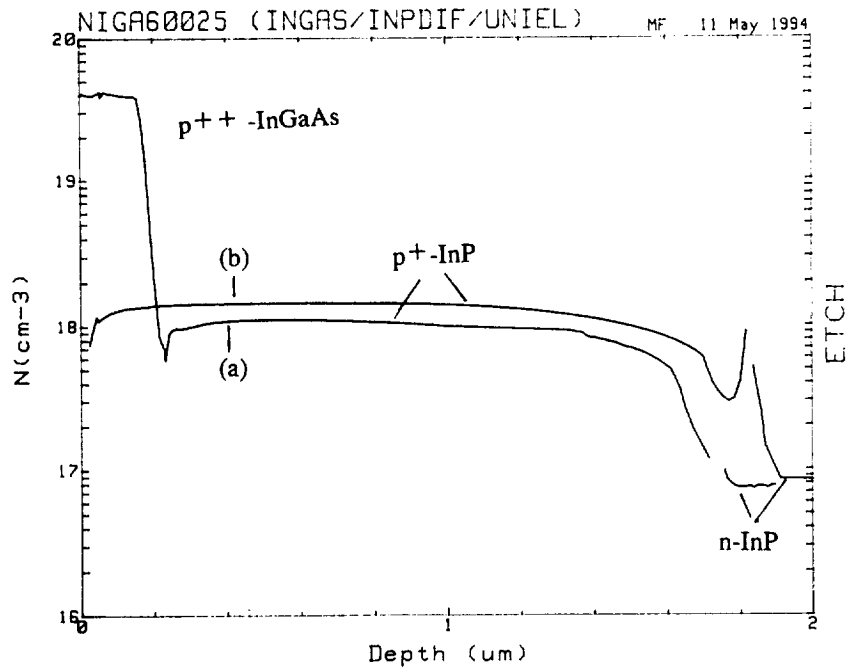


Fig.7. EC- V profiles of p^+n (Cd,S) InP structures, diffused in similar conditions at 600 °C through: (a) undoped InGaAs, and (b) $\text{In}(\text{PO}_3)_3$ cap layers.

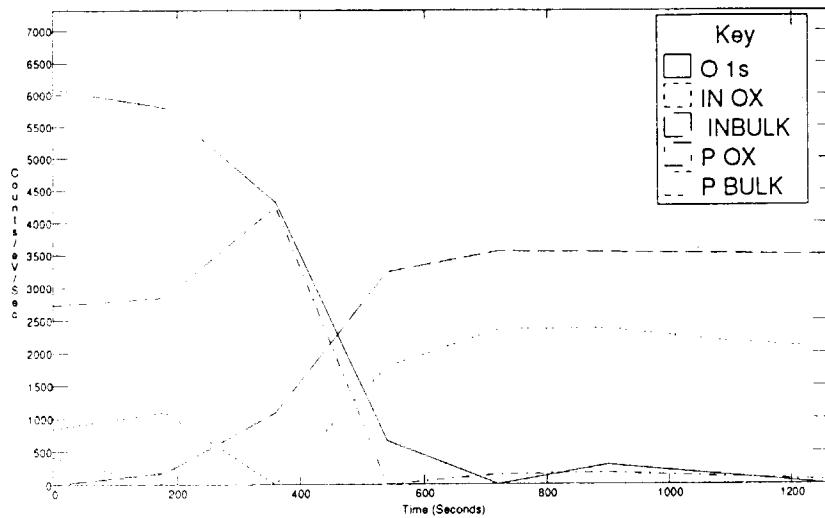


Fig.8. XPS profiles of an oxide grown on InP using the PNP etch.

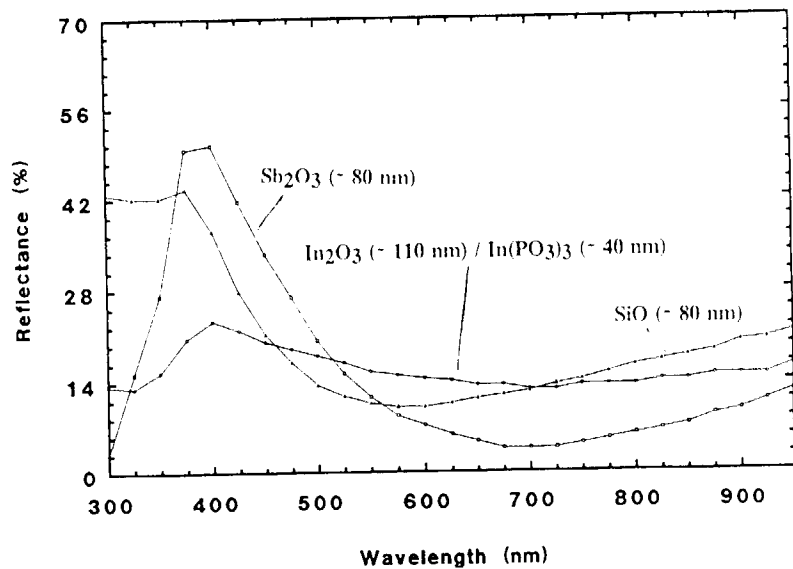


Fig.9. Surface reflectance of p^+n InP using a single layer AR coating.

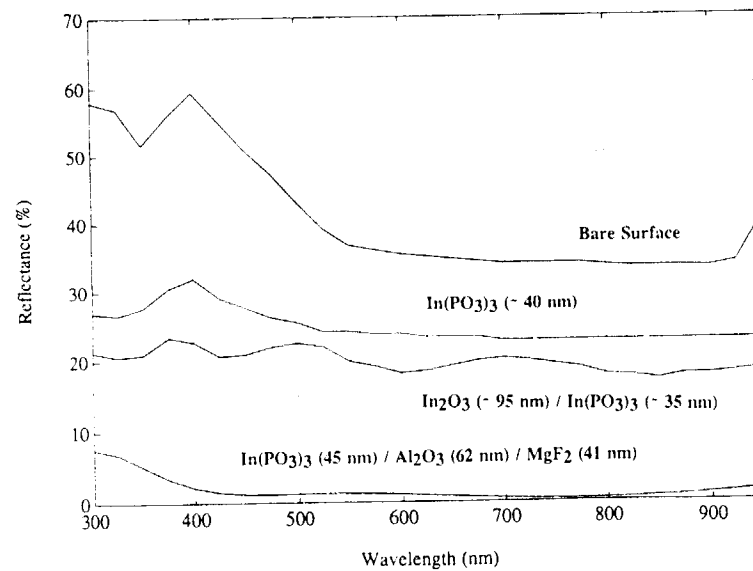


Fig.10. Surface reflectance of p^+n solar cells using a double or single layer chemical oxide as compared to a bare surface and optimized three layer AR coating.

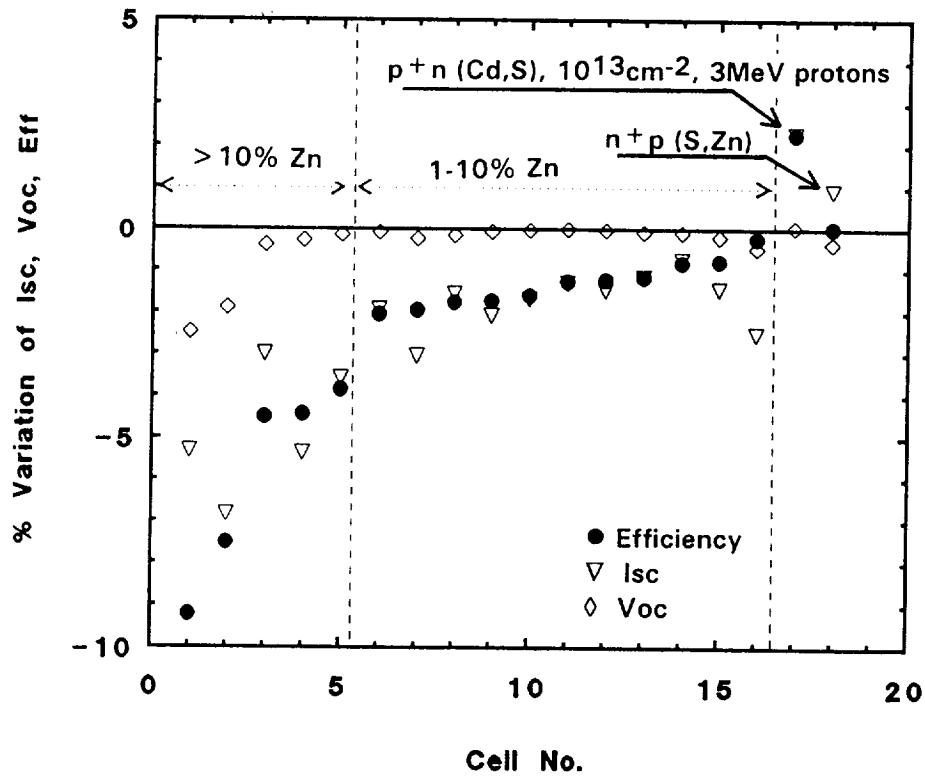


Fig.11. Relative degradation of p^+n (Cd,S) InP (cells # 1-17), and n^+p (S,Zn) InP (cell #18) parameters after 1 hour AM1.5, 25 °C illumination. For cells # 1-16, the Zn-content of evaporated Au-Zn front contacts is shown.

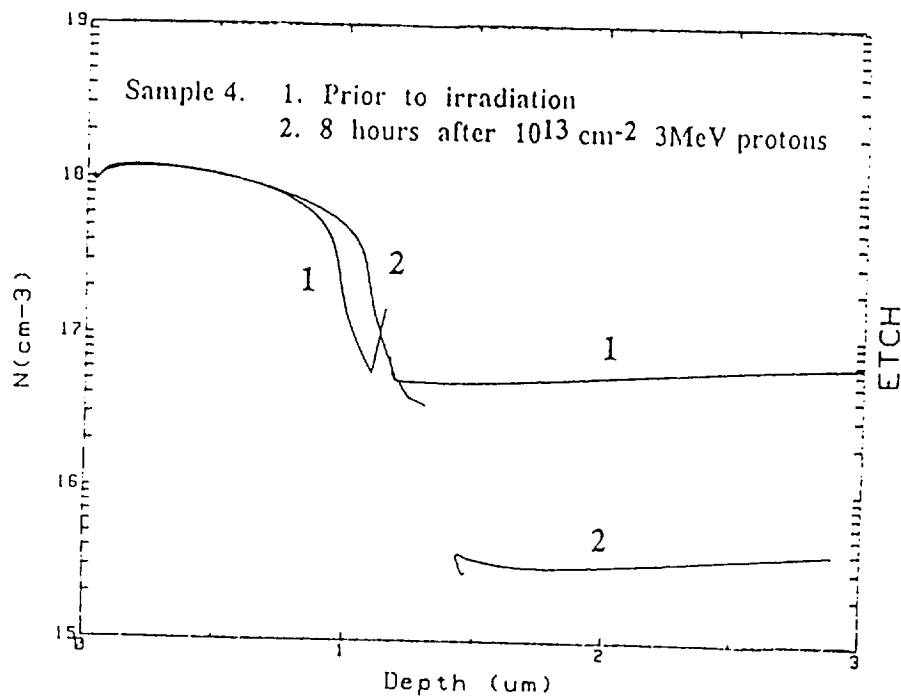


Fig.12. EC-V profiles of a p^+n (Cd,S) InP structure, prior to and after 10^{13}cm^{-2} 3 MeV protons irradiation.

Fig. 13. Processing scheme of high efficiency p^+n (Cd,S) InP diffused-junction solar cell.

