Recent Advances in the ITO/InP Solar Cell*

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Introduction

InP based solar cells have become important for space applications in recent years due to their combination of radiation resistance and high efficiency [refs. 1-2]. Although the highest efficiencies (> 18% AM0) have been achieved through epitaxial growth of homojunction cells, remarkable performance of 17.0% AM0 and radiation hardness have been achieved with indium tin oxide (ITO)/InP cells [refs. 3-4]. In this later cells design, the ITO is sputter deposited, onto a crystalline InP p− base substrate, at room temperature, using either RF or DC magnetron sputtering of an In2O3/SnO2 composite target. In addition to its relative simplicity, this technique can be easily scaled to produce the 4 cm² cells necessary for flight experiments.

During past studies, several noteworthy observations have been made which have led to either improved device performance, or a greater understanding of the device operating principles. Some of these observations are: [refs. 4-6] 1) The top surface of the p− InP is type converted during the ITO sputter deposition process resulting in a junction which demonstrates homojunction behavior, 2) The device characteristics (notably the open circuit voltage [Voc]) can be increased through the use of an epitaxially grown p− base layer (i.e., "hybrid" cells), 3) The type conversion and device performance is enhanced further through the incorporation of H₂ into the sputtering gas mixture and, 4) After the deposition process, Sn is observed to have diffused into the InP bulk. Although all these observations are still valid, several more can now be added to the list as will be described.

The first of these new observations involves the choice of substrate. As stated above in observation 2, efficiency improvements were realized when the bulk p− InP substrate was replaced with a p+ substrate which had been specially prepared with an epitaxially grown p− base layer (hybrid cells). Although this technique resulted in very efficient cells and also enabled optimum base doping level studies, the epitaxial growth step complicated an otherwise simple junction formation procedure. Thus, efforts have continued to take what was learned with this hybrid cell study and use it to improve the simpler ITO/InP cell design utilizing bulk p− InP substrates. Currently, although the best ITO/InP cell made to date is still a hybrid structure, cells can now be made on bulk material which are of virtually identical quality.

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The second continuing area of study involves the more fundamental question of what actually happens during the ITO sputtering process. Although, at present, this area is viewed more as pure science rather than solar cell technology, it is believed that only by thoroughly understanding this aspect of junction formation will insight to future cell improvements be acquired. Thus far, attempts to identify the mechanism of type conversion unambiguously have met with only limited success. The most recent example of this involves the above observation 4 in that, for a considerable time, it was believed that indiffusion of Sn was the most probable cause of type conversion. With this in mind, a series of experiments involving the sputter deposition of (Sn free) In$_2$O$_3$ (IO) was performed. The (unexpected) result of this experiment has made it necessary to question whether Sn is the cause of type conversion, and to consider more seriously the possibility that “sputter damage” may instead be the dominant mechanism.

The final area of recent studies involves measuring the stability of the ITO/InP cells over a period of about a year. This study was enabled by the development of a highly durable top contact grid metallization, necessary for long term grid integrity. The new contact procedure replaces the plated Au contacts with a metallization stack composed of Cr, Pd and Au which provided the necessary components of adhesion, diffusion barrier and conduction layers respectively. This contact proved so durable that the previous difficulties with contact adhesion loss have been completely eliminated.

Experimental

As mentioned in the past, one of the single most important elements of producing high efficiency ITO/InP solar cells is the preparation of the InP substrate before ITO deposition. Since this cell is formed by the sputter deposition interacting with the near surface ($<0.1 \mu m$) of the InP substrate, all techniques we have used to prepare the InP have one goal in mind: to produce InP surfaces with are of both reproducible and high quality. Although these goals are difficult in themselves, they are further complicated by the fact that, due to the high temperature necessary to form the ohmic back contact, this contact must be made before junction formation, thereby subjecting the untreated front surface to, possibly damaging, thermal effects. In an effort to satisfy these conflicting criteria, three main approaches to cell fabrication have been (historically) developed: These are: 1) Using p$^-$ bulk substrates and chemo-mechanically repolishing the front surface after back contact formation thereby polishing away any suspected thermal damage. 2) Using p$^+$ substrates with an epitaxially grown p$^-$ base layer. Although this structure is rather complicated, it has the combined benefits of lower bulk resistance, lower back contact formation temperature and a very high quality and controllable base layer. 3) Using high quality p$^-$ bulk substrates, but forming the back contact at the lowest possible temperature thereby avoiding the need for chemo-mechanical repolishing of the front surface. It
is this final technique which has been used extensively for the cells described in this paper.

The p- InP bulk substrates, from Nippon Mining Co. Ltd., are of carrier concentration 1.6 - 2.5 \times 10^{16} \text{ cm}^{-3}, Zn doped and of (100) orientation. Before back contacting, they are typically cleaved to size on which either about eight - 0.1 \text{ cm}^2 cells or one - 4.0 \text{ cm}^2 cell (2 \text{ cm} \times 2 \text{ cm}) can be fabricated. Back contacting is a two-step process involving first the resistive vacuum evaporation of Au/Be (1 w% Be, available from Metron Inc.), sintering on a graphite strip heater at 375 - 395°C for approximately 30 sec. in forming gas (10% H_2:90% N_2), etching in a concentrated H_2O:NaOH solution and plating with high purity Au. The specific details are explained elsewhere [ref. 7].

For sputter deposition of the ITO and IO (and thus the junction formation), a 2 inch planar US Gun is used in DC magnetron mode in a sputter-up orientation. In order to improve junction quality, the initial \sim 5 \text{ nm} of ITO or IO is deposited in a H_2 rich atmosphere, while the remaining \sim 50 \text{ nm} is deposited in a more conventional oxygen rich environment (leading to improved transmittance) [ref. 4]. The operating parameters are typically 300-400 Volts and 0.05-0.15 Amps, resulting in a deposition rate of \sim 0.01 \text{ nm sec}^{-1}, for H_2 rich material and \sim 0.05 \text{ nm sec}^{-1} for oxygen rich material, at \sim 14 \text{ cm} in front of the target. The targets (purchased from KEMA, Fallbrook, CA) are made from 99.99% pure In_2O_3 and 99.9% pure SnO_2, the ITO mixture being 91:9 molar percent respectively. Predeposition is normally done for \sim 3 min. with the substrate shuttered. The InP substrate is not heated or cooled during deposition.

Although the deposition is primarily done in Ar (\sim 5 \times 10^{-3} \text{ Torr}), both O_2 and H_2 are added to predetermined partial pressures of \sim 2 \times 10^{-5} \text{ Torr} and 1 - 8 \times 10^{-4} \text{ Torr} respectively. All gases are UIIP grade and the flow is controlled with needle valves. The O_2 and H_2 pressures are set with an ion gauge, while the Ar pressure is set with a Convelectron gauge. The vacuum system is a Perkin Elmer ULTEK ACRS equipped with both a cryogenic and a turbomolecular/mechanical pump. Although base pressures in the range of \sim 1 \times 10^{-7} \text{ Torr} are attainable with the cryo pump, the turbomolecular/mechanical pump configuration, having a base pressure of \sim 1 \times 10^{-5} \text{ Torr}, is normally used during sputter deposition.

After ITO deposition, individual cells are formed. Two different photolithographic patterns of different nominal areas as mentioned above are used. Top contact metallization was performed via a two step process involving first the E-beam deposition and photolithographic lift-off of 80 nm of Cr and 40 nm of Pd (adhesion layer and diffusion barrier respectively) and, second, the over-plating with \sim 6 \text{ nm} of high purity Au (conduction layer) [ref. 7]. Electrical isolation of the cells was done by photolithographically defined mesa etching using HCl. After the cells were formed, a nominally 77 nm thick MgF_2 coating was applied, thereby creating an optimized two layer MgF_2/ITO antireflection coating [ref. 8].
The electrical characterization of the cells consisted of both light and dark current-voltage measurements, quantum efficiency measurements and capacitance-voltage measurements. For the light current-voltage measurements, two different solar simulators were used. For primary measurements (Figures 1, 4 & 6), standard solar cell efficiency measurement procedures were employed [ref. 9], while, for the variational analysis of the short circuit current ($J_{sc}$) and $V_{oc}$ (Figure 7), a different simulator was used. Although the output of this second simulator was adjusted to simulate currents as near as possible to those obtained on the primary simulator, these values should not be considered absolute. Additionally, for the variational analysis of $J_{sc}$, a correction for the effect of ITO and IO thickness variations was done using a computer simulation which, by incorporation of the quantum efficiency of the cell, the necessary optical parameters of the layers in the antireflection coating stack and the appropriate solar spectrum, resulted in a normalization of the $J_{sc}$ to a constant (50 nm) ITO thickness [ref. 8]. Depth profiling of the electrical characteristics of the type converted region was performed using a spreading resistance technique (Point Contact Current Voltage [PCIV] method) provided through collaboration with Solid State Measurements, Pittsburgh, PA [ref. 10].

Optical measurements (thickness and refractive index) were performed with a Rudolph Research Ellipsometer operating with a HeNe laser.

**Results and Discussion**

**Bulk ITO/InP Cells**

As mentioned above, the best efficiency ITO/InP devices have been produced using the hybrid structure in which the ITO is deposited onto a high quality epitaxially grown p− base layer. Although these cells resulted in 17.0% AM0 efficiency, they lacked the simplicity of earlier structures in which the ITO was deposited directly onto bulk p− InP substrates (i.e., InP which did not have an epi layer base). Recently, however, results from cells made with bulk substrates have indicated that, if cell fabrication and processing are carefully controlled, bulk cells of essentially identical efficiencies to their hybrid counterparts can be made (See Figure 1).

There are several reasons for the recent success in using bulk InP which are not immediately obvious. First, it has been determined, if sufficient temperature control is achieved, then the back Au/Be ohmic contact can be formed without damage to the front InP surface. This, in turn, makes repolishing of the front InP surface unnecessary and subsequently increases the reproducibility of the surface quality before deposition. Specifically, the contact will form between ~365°C and ~375°C, yet surface damage is not detected until ~405°C [ref. 7]. Secondly, if InP substrate material is acquired from a select group of vendors, then the as-received surface quality appears to be only slightly worse than that which can be made with APMOVPE growth. Additionally, although it is true that the series resistance will be increased if
the p+ substrate is replaced by p− material, measurable reductions in the fill factor (FF) due to the p− substrates have not been observed. Indeed, the fill factors of the bulk cells are often slightly higher than those measured for the hybrid cells. This artifact may, however, be due to the higher quality of the Cr/Pd/Au top grid metallization, which had not been developed at the time of the hybrid cell study. Finally, it appears that the addition of H2 to the sputtering gas is of even greater benefit to the bulk cells than it was found to be for the hybrid cells. Since this process appears to passivate both deep and shallow acceptors to a significant depth, it not only improves the dark characteristics (and thus the Voc and FF), but also, in the case of the bulk cells, significantly improves current collection in the base. Specifically, the Voc is increased by ~50-60 mV and the FF is increased by ~5-7% (apparent increase in shunt resistance). Although the Jsc should increase due to the improved long wavelength collection (See Figure 2), since the H2 rich ITO layer is of such poor optical quality, the gains due to increases in quantum efficiency (QE) are presently being offset by increased absorption losses in the ITO. Presently, work is proceeding to minimize or eliminate this absorption loss.

There are several fundamental observations which can be drawn from comparisons of the bulk vs hybrid ITO/InP cells. The first is that it appears once type conversion has been effected, then the minority carrier lifetime in the hybrid cells is slightly better than in the bulk cells. Evidence of this is the slightly higher Voc of the hybrid cells (15-20 mV). Unfortunately, this difference in Voc is so small that comparisons of dark I-V measurements are not conclusive. Additionally, capacitance-voltage (C-V) measurements indicate further that this Voc difference is not due simply to the higher value of NA in the hybrid cells (See Figure 3). On the contrary, analysis of hybrid cells indicates a trend of higher Voc as NA decreases. Although this observation is not yet fully understood, it may be due to increases in the minority carrier diffusion length in the base as NA decreases. Also, although this general trend of higher Voc with lower NA may be equally true for bulk material, the measured Voc of the bulk cells (NA ≈ 5 × 10^16 cm^-3) are much lower than would be extrapolated from base doping studies done with the hybrid cells. Thus, there appears to be an added degree of quality in the epitaxially grown material which leads to slightly higher Voc. Although, if the parameters leading to this difference could be understood, further improvements in Voc would possibly follow, it should nevertheless be stressed that the bulk and hybrid cells are very similar, indicating that the passivation/compensation effects of sputtering in H2 do indeed create very similar type converted regions.

Large Area ITO/InP Cells

Another aspect of bulk vs hybrid comparisons is that the sputtering / hydrogenation process appears relatively insensitive to surface irregularities of the bulk substrates. This is noted by observing that if several cells are made on a single p− bulk InP substrate, the Voc does not vary greatly between cells located at different
parts of the substrate (the $J_{sc}$ will vary slightly, however, due to ITO thickness variations). This can be compared to hybrid cells where, if an epitaxial growth-related defect is present, then the characteristics of the particular cell containing this defect often would be very poor. Thus, it is the degree of spatial uniformity of the epitaxial growth which limits the performance of large area hybrid ITO/InP cells. However, with the combined observations that high-efficiency cells could be made directly from as-received bulk InP substrates, and the inherent spatial uniformity of the sputter-formed homojunction, the opportunity to fabricate large area ITO/InP cells was immediately presented. Using the same technology explained above, cells with a total area of 4 cm$^2$ were fabricated. Although these cells lacked an optimum grid design, they demonstrated nearly 17% (Global) efficiency (see Figure 4), thereby not only supporting the above observation concerning the spatial uniformity of the type conversion process, but also greatly supporting earlier speculation about the ease of scaling this technique for production purposes. Furthermore, examinations of the $V_{oc}$ and the QE of these first large area cells indicates that, once these cells are optimized, the resultant efficiency should be very near to that which has been (thus far) achieved with smaller cells (~17% AM0).

**IO/InP vs ITO/InP Cells**

As mentioned above, it was believed for several years that the Sn played an active role in the type conversion of the InP surface during sputtering, thereby forming the InP homojunction of the ITO/InP cell. This was supported primarily by secondary ion mass spectroscopy (SIMS) analysis which showed Sn penetration to about 100 nm into the InP after the ITO deposition [ref. 5], and by a spreading resistance technique (PCIV) which showed electrical type conversion to roughly the same depth (see Figure 5). Furthermore, experiments to assess the role of “sputter damage” suggested that this mechanism alone did not produce strong type conversion or good quality cells. With these observations in mind, it seemed probable that if Sn free IO/InP cells were made, than they would demonstrate very poor device quality (low $V_{oc}$ and $J_{sc}$), thereby further proving the crucial role of the Sn species. However, this was not the observed result.

As shown in Figure 6, the IO/InP cells demonstrated remarkably good performance of nearly 17% (Global) with $V_{oc}$ within a few millivolts of their ITO/InP counterparts. Additionally, since the same sputter conditions were used for the IO as those used for the ITO, the IO optical quality is dubious and, as can be inferred from Figure 7, it is likely that if the IO transmittance were improved, the $J_{sc}$ of these cells may indeed be equivalent to that of the ITO cells.

The fact that the IO cells demonstrated such similar quality to the ITO cells strongly suggests that the Sn in the ITO is not the essential part of type conversion as it was previously believed to be. The IO result also indicates that the previous conclusion about the limited effect of “sputter damage” is probably in error, and that
deposition-related (and not Sn-related) effects are very important to the type conversion process. Currently, work is proceeding to determine whether "sputter damage" may manifest itself by causing the InP to lose P from the bulk (these vacancies might then act as donor states, assisting type conversion).

Initial Stability Studies

Finally, since the Cr/Pd/Au contact is very adherent and durable, initial stability studies have been conducted during the past year. Although it should be stressed that, thus far, data has been collected on only two cells (two - 0.1 cm², bulk ITO/InP cells on a single substrate), the results are very encouraging. In Figure 8 are shown results indicating that, within experimental uncertainty, the J_sc and the FF are stable. The V_oc is shown to decrease linearly at a rate of about 8 mV per year. However, this reduction occurred while the cells were stored under dim light conditions and, as shown in Figure 9, the original V_oc is quickly restored when the cells are light-soaked at V_oc for several hours (for example, in an XT-10 solar simulator set at ~AM1.5). From these observations, it is believed that, if the cells had been securely mounted in a durable test structure and if they had been continuously operated between successive measurements, no V_oc reduction would have been observed and the efficiency would have been stable.

Conclusions

It has been demonstrated that ITO/InP solar cells can now be made on as-received p⁻ bulk substrates which are of nearly equal quality to those which could previously only be made on epitaxially grown p⁻ InP base layers. Although this advancement is due in part to both increases in substrate quality and a better understanding of back contact formation, it appears that the passivation/compensation effects resulting from having H₂ in the sputtering gas tends to reduce significantly the performance differences previously observed between these two substrates.

It is shown that since high efficiency ITO/InP cells can be made from as-received substrates, and since the type conversion process is not highly spatially dependent, large area ITO/InP cells (4 cm²) with efficiencies approaching 17% (Global) can be made. Furthermore, the measured V_oc's and QE's from these large cells suggest that, when they are processed using optimum grid designs, the efficiencies will be nearly equal to that of the smaller cells thus far produced (i.e., ~17% AM0).

It has been shown, through comparative experiments involving ITO/InP and IO/InP cells, that Sn may not be the major cause of type conversion of the InP surface and thus further implies that the ITO may not be an essential element in this type of device. Specifically, very efficient photovoltaic solar cells have been made by sputtering (Sn free) In₂O₃ showing that type conversion and subsequent junction formation will occur even in the absence of the sputtered Sn species. This result
suggests that "sputter damage" (P depletion and/or H₂ incorporation) may indeed be the important mechanism(s) of type conversion.

Finally, an initial study of the stability of the ITO/InP cell done over the course of about one year has indicated that the J_sc and the FF are measurably stable within experimental uncertainty. Also, although the V_oc does decrease linearly at a rate of about 8 mV per year if the cell is kept in the dark, the original V_oc of the cell is quickly restored if the cell is light soaked. It is therefore believed that, if the cells were continuously operated between successive measurements, this V_oc reduction would not be observed and the overall efficiency of the cells would be stable.

References


Figure 1. Current-voltage characteristics of the best ITO/InP cell made to date from bulk InP p material (i.e., the ITO is sputter deposited directly onto as-received InP substrates, no epitaxially grown base layers). These characteristics are measured under standard Global and AM0 reporting conditions (however, the AM0 measurement is not confirmed at NASA). Cell temperature = 25°C, total area = 0.108 cm².

Figure 2: External/Internal quantum efficiencies (QE’s) for the device in Figure 5. (a) External QE for cell with 50.7 nm of ITO only, (b) with additional 75.0 nm of MgF₂ coating and (c) internal QE of the same device. Note this device demonstrates an internal QE of >90% over a substantial portion of the spectral range. Note particularly the high collection at long wavelengths indicating the passivation effect of the H₂ in the sputtering gas.
Figure 3: Plot of data from capacitance-voltage measurements. The circles indicate the values of $N_A$ for a series of hybrid cells made with three nominally different values of (epitaxial) base doping (base thickness noted next to corresponding data). The dashed line indicates trend of increasing $V_{OC}$ with decreasing $N_A$. Note also that the $V_{OC}$ of the bulk cell (as indicated by the cross) does not fall on the same trend as the hybrid cells.

Figure 4: Current-voltage characteristics of a 4 cm$^2$ ITO/InP cell (a) before and (b) after MgF$_2$ deposition. These measurements are performed under standard Global reporting conditions. Although this cell lacked an optimized grid design, it demonstrated performance attesting that this technique can be easily scaled.
Figure 5: Carrier concentration vs depth profile resulting from a Point Contact Current Voltage (PCIV) Spreading Resistance technique. (a) Illustrates the type conversion of a semi-insulating (Fe doped) InP substrate due to the sputter deposition (in H$_2$) of 5 nm of ITO. Note that in this case, $8 \times 10^{13}$ cm$^{-3}$ is the lower limit of the PCIV technique. (b) Illustrates the same profiling technique applied to an actual bulk ITO/InP solar cell in which the ITO was sputter deposited (H$_2$ partial pressure $\sim 2 \times 10^{-4}$ torr) onto a p- (Zn: $2 \times 10^{16}$ cm$^{-3}$) InP substrate. In both cases, the ITO was removed by chemical etching in 1000 H$_2$O:HF before PCIV profiling. The vertical dashed line at about 70 nm indicates the approximate depth of type conversion. These data were fitted by assuming Hall mobilities for the n and p regions of 100 and 120 cm$^2$ V$^{-1}$ sec$^{-1}$ respectively.
Figure 6: Comparison of the current-voltage characteristics of an IO/InP and an ITO/InP cell. Note that, even though only a few IO/InP cells were made, and thus the junction fabrication was not optimized, these cells are remarkably similar. This strongly suggests that, contrary to earlier speculation, Sn incorporation into the InP is not the main cause of type conversion. Note also that, although at the time of fabrication the efficiency of these IO/InP cells was 16% - 17% (Global), the above measurement, taken under standard reporting conditions, was not performed until over six months later, during which time the $V_{OC}$ and the fill factor had each degraded slightly, resulting in lower measured efficiencies. Cell temperature = 25°C, cell area = 0.108 cm$^2$. IO (and ITO) and MgF$_2$ thicknesses are ~50 nm and ~70 nm respectively.

Figure 7: Illustration of the dependence of $V_{OC}$ and $J_{SC}$ on hydrogen partial pressure for both ITO (solid line) and IO (dashed line) solar cells made on bulk substrates. Although the main feature of this comparison is that the Sn (present only in the ITO/InP cells) is not necessary to produce homojunction like behavior, one notes that both the $V_{OC}$ and the $J_{SC}$ are lower in the IO/InP cells. Furthermore, unlike the $J_{SC}$ in the ITO/InP cells which is seemingly insensitive to hydrogen partial pressure, the $J_{SC}$ of the IO/InP cells demonstrate considerable sensitivity to this parameter. These data were collected for 0.108 cm$^2$ cells using an XT-10 solar simulator referenced to a Global (1000 W m$^{-2}$) reference spectrum using a Si reference cell. The error bars on the $J_{SC}$ represent the changes in $J_{SC}$ which would be expected from a ± 2.5 nm variation in ITO thickness.
**Figure 8.** Diagram illustrating successive measurements of the light I-V characteristics of an ITO/InP cell during the year after fabrication. Note that, within experimental uncertainty, the Jsc is stable. It is also believed that the slight reduction in fill factor is an artifact of a progressively dirty back contact rather than a junction effect. The apparent reduction in Voc is, however, a real effect (and equates into a reduction in efficiency). This reduction however appears to be only an artifact of the cell being kept in a dark location between measurements, the original Voc being restored when the cell is operated (see Fig. 9).

**Figure 9.** Diagram illustrates the improvement of the Voc as the ITO/InP cell shown in Fig. 8 is light soaked at ~AM1.5. Note the two different time scales on the horizontal axis.