A DETAILED STUDY OF THE PHOTO-INJECTION ANNEALING
OF THERMALLY DIFFUSED InP SOLAR CELLS

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ABSTRACT

A detailed analysis of the annealing of thermally diffused InP solar cells fabricated by the Nippon Mining Co. is presented. The cells were irradiated with 1 MeV electrons, and the induced degradation is measured using deep level transient spectroscopy and low temperature (86 K) IV measurements. Clear recovery of the photovoltaic parameters is observed during low temperature (T < 300 K) solar illuminations (1 sun, AM0) with further recovery at higher temperatures (300 < T < 500 K). For example, the output of a cell which was irradiated up to a fluence of 1×10^{16} cm^{-2} was observed to recover to within 5% of the pre-irradiation output. An apparent correlation between the recovery of I_{sc} and the annealing of the H4 defect and of the minority carrier trapping centers is observed. An apparent correlation between the recovery of V_{oc} and the annealing of the H5 defect is also observed. These apparent correlations are used to develop a possible model for the mechanism of the recovery of the solar cells.

INTRODUCTION

It is well known that single crystal InP solar cells not only display record high beginning of life efficiencies but also display a resistance to irradiation which is superior to that of Si and GaAs cells (ref.1-3). Furthermore, it has been shown by Yamaguchi et al. that InP solar cells grown by thermal diffusion rapidly recover the radiation-induced degradation under solar illumination (ref 3). However, it has also been shown that InP cells grown by MOCVD, while exhibiting a marked decrease in the radiation-induced defect concentration due to photo-illumination, display no corresponding recovery of the solar cell output (ref 1). Although much detailed information has been obtained about the behavior of MOCVD InP solar cells, the published data on diffused junction cells is not complete enough to understand the observed different behavior. This paper presents new results on the recovery of irradiated, diffused junction InP cells which enable further conclusions to be drawn.

A major difficulty is that to determine the radiation-induced solar cell degradation, one must illuminate the cell with simulated solar light which is capable of annealing the thermally diffused cells. To avoid this annealing, the samples here were held at 86 K during the IV measurements. DLTS measurements before and after an IV measurement showed that the solar illumination at 86 K does not anneal the cell. Furthermore, repeated IV measurements at 86 K showed no recovery in the solar cell output. Effectively, any photo-injection annealing of the cells has, therefore, been "frozen out" at 86 K.

A related problem exists in the measurement of the minority carrier trapping centers by the DLTS technique. For DLTS to detect minority traps, minority charge carriers must be injected into the depletion region.

This is commonly done by applying a forward bias fill pulse to the sample during the measurement. However, since this establishes a current through the junction, it causes injection annealing of the defect spectrum (ref 1). In the present experiments, this effect is avoided by creating electron-hole pairs in the depletion region by pulsed laser excitation. The junction field quickly separates the charges, leaving the minority carriers available for capture at a defect level. In this way, the minority trapping centers can be detected without annealing the sample.

The present study determines the changes in the radiation-induced defect spectrum associated with the annealing stages of the irradiated solar cell IV curves. This is accomplished by measuring the DLTS spectrum of the actual solar cells after each annealing step. The results provide insight into the response of InP solar cells to a harsh space radiation environment which was previously unavailable. It is detailed investigations like this which will allow a full exploitation of the unique qualities of InP solar cells.

EXPERIMENTAL NOTES

The samples studied in this research are InP solar cells grown by the Nippon Mining Co (ref 4). They are the NS12B type. The initial cell dimensions were 1cm x 2cm x 400μm. The cells have a SiO$_2$/ZnS antireflective coating. The shadow loss is stated by the manufacturer to be approximately 5%. The cell specifications indicated efficiencies of 16.2 % (AM0, 25° C), short circuit currents (I_{sc}) of 64.3 mA, and open circuit voltages (V_{oc}) of 0.823 V. The cells are n$^+$p junctions, so a positive DLTS signal (which indicates a majority carrier trap) signifies the capture of holes. A negative signal (which indicates a minority carrier trap) signifies the capture of electrons.

In order to mount these cells into the DLTS cryostat used in the present research, it was necessary to reduce the size of the cells. This was done by sawing the cells into 0.4 x 1 cm pieces. This had little effect on the short circuit current density and the open circuit voltage. Unfortunately, the sawing introduced a series resistance into the cells which reduced the fill factor and the efficiency of the samples. This is most likely due to dislodging the metalization grid of the cells. Therefore, the present study concentrates on changes in I_{sc} and V_{oc} and avoids any discussion of the efficiency.

The IV measurements were made under 1 sun, AM0 conditions at 86 K. The simulator used was an Oriel, 1000 W Xe arc lamp, portable solar simulator. The DLTS equipment used was a Bio-rad DL4600 Deep Level Transient Spectrometer. All the DLTS measurements were made with a -2 V reverse bias. The 1 MeV electron irradiations were performed at the National Institute of Standards and Technology (NIST). A Faraday cup was used for dosimetry. The fluences were determined to an accuracy of about 15%.

EXPERIMENTAL RESULTS

Prior to irradiation, one minority carrier trapping center was detected in the InP solar cells (dashed line in figure 1), and no majority carrier trapping centers were evident. The activation energy of minority trap was found to be about 0.32 ± 0.01 eV below the conduction band. This energy is close to that of the defect labeled ED, measured in electron irradiated MOCVD InP (ref 1), so a tentative identification with that defect is made here.

The defect spectrum induced by 1 MeV electron irradiation is indicated by solid lines in figure 1. The electron fluence was 6×10^{15} cm^{-2}. Except for the relatively weak EE and EF signals, this spectrum is virtually identical to that measured on irradiated MOCVD InP (ref. 1), so the defects are labeled accordingly. This data shows a clear resemblance between the minority trap measured before irradiation and the ED defect. Note that the signal of H5 and of all the minority traps is multiplied by 10 to make them more visible. Also, since the negative DLTS signal is most clear after the positive signal has been removed, the minority trap spectrum shown was measured on a cell which had been annealed at 500 K for 1 hour under 1 sun, AM0 illumination. The EC,EA, and ED centers were evident directly after irradiation and before annealing of the cells. However, the EE and EF centers were not detected until the H4 and H5 centers had been substantially annealed.

Since the EE and EF signals are weak and located directly below the H4 and H5 peaks in the spectrum, their detection is difficult. A full investigation of their properties will be reported later. The H3 defect level is not discussed in detail for similar reasons. Because the H3 defect is so close to H4 in the spectrum, it is difficult to monitor.
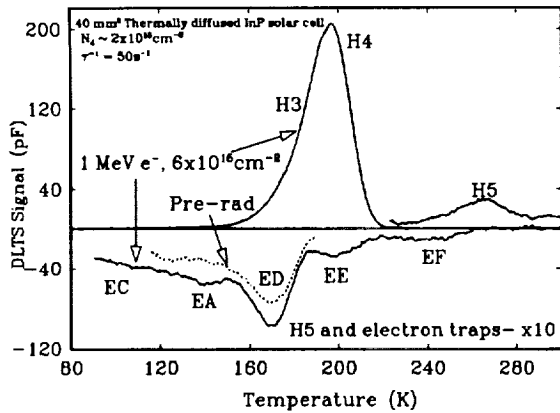
Figure 1: Radiation-induced defects in thermally diffused InP solar cells. The defects are labeled according to ref. 1. The H5 and the minority carrier trap signal is multiplied by a factor of 10.

The first experiment was an isochronal annealing experiment. A cell which had been irradiated with 1 MeV electrons to a fluence of 1×10^{15} cm^{-2} was illuminated for 1 min under 1 sun, AM0 simulated solar light at increasing temperatures. During illumination, the cell was short-circuited through an ammeter. After each illumination, the majority carrier defect spectrum was measured along with the IV curve (at 86 K). The results are shown in figures 2 and 3. The height of the DLTS peak is directly proportional to the defect concentration. The photovoltaic (PV) parameters of figure 2 are normalized to their pre-rad values, while the peak height of H4 is normalized to its maximum value, measured directly after irradiation. V_{oc} was essentially unaffected by the irradiation. I_{sc} and P_{max} are degraded slightly and display a clear annealing stage at 175 K. At the same time, the H4 peak is seen to essentially disappear. Next, an isothermal photo-injection annealing experiment was performed. A cell which had been irradiated with 1 MeV electrons up to a fluence of 3×10^{15} cm^{-2} was short-circuited and illuminated under 1 sun, AM0 at 225 K.
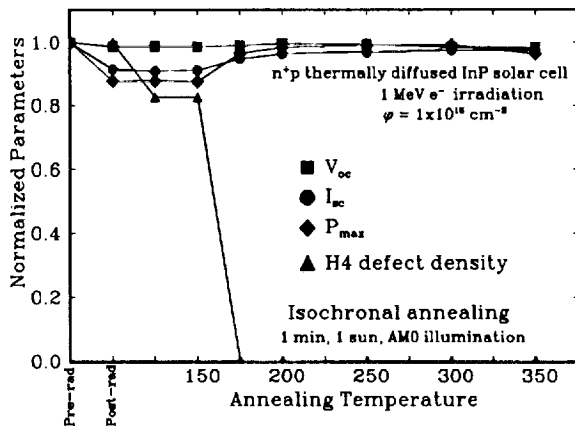

Figure 2: The annealing induced in a thermally diffused InP solar cell by solar illumination. The PV parameters are normalized to their pre-rad values and the H4 defect density to its maximum value.
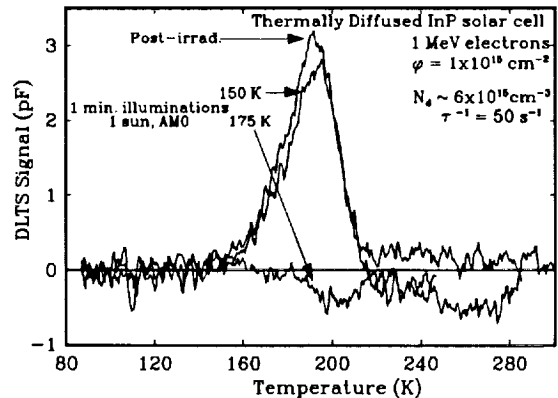

Figure 3: The photo-injection annealing of the H4 defect in the solar cell of figure 2.

Both majority and minority trap spectra were measured along with the IV curves (at 86 K). The results are shown in figures 4 and 5. The irradiation degraded V_{oc} from 1.198 V to 1.151 V. The photo-injection had no affect on V_{oc}. The irradiation degraded I_{sc} by about 8%, but an hour of illumination induced almost full recovery. An hour of illumination is seen to almost completely remove the H4 defect as well. However, the concentration of the H5 defect does not change during the experiment. The concentration of the ED defect seems to increase, but since the minority trap spectrum in figure 5 is multiplied by 5 to make it visible beneath the H4 signal, any apparent changes in the ED peak height are quite small relative to the H4 signal. H5 is not scaled in this figure.

A second isothermal annealing experiment was done on a cell which had been irradiated up to a fluence of
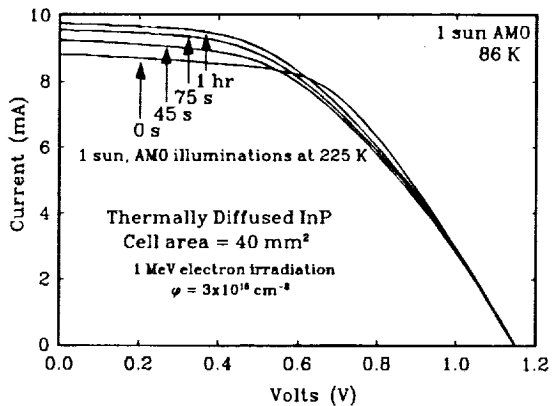
Figure 4: The isothermal, photo-injection annealing of the IV curves of an irradiated InP solar cell. The illuminations cause an increase in I_{sc} but not V_{oc}.
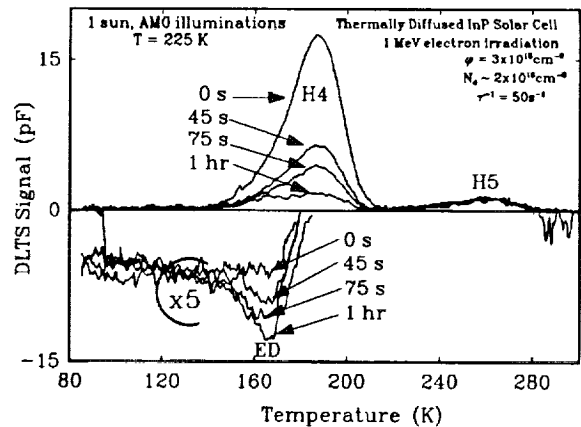
Figure 5: The photo-injection annealing of the DLTS spectra of the cell of figure 4. The electron trap signal is multiplied by 5. The H4 defect concentration decreases but H5 is unchanged.

1×10^{16} cm^{-2}. The illuminations were done at 275 K for cumulative times up to 4.25 hours. The results are shown in figure 6. The open symbols on the left hand vertical axis of figure 6 are the pre-rad values for the PV parameters. The open symbols on the right hand axis are the values of the PV parameters after 4.25 hours of illumination. This is a revealing set of data because the high fluence has caused a significant degradation in all of the PV parameters, so the recovery under illumination is quite clear. Each parameter shows steady recovery for the first 25 minutes of illumination. After 25 minutes, the recovery continues but at a much slower rate. It seems that there is an asymptotic limit to the recovery.
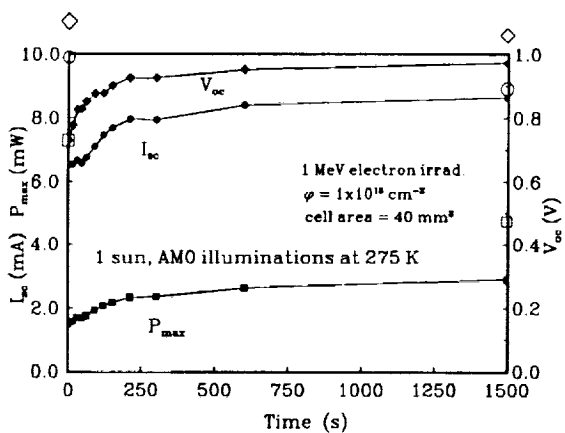

Figure 6: The annealing of a heavily irradiated InP solar cell. The open symbols on the right vertical axis are the BOL values while on the left axis are the values after 4.25 hours of annealing.

To investigate this asymptotic limit, after the 4.25 hours of illumination at 275 K, the cell was illuminated at progressively higher temperatures. Illumination for 30 minutes at 300 K and one hour at 373 K induced further recovery in V_{oc} but none in I_{sc}. Illumination for 1 hour at 450 K caused a large increase in the entire IV curve (figure 7). This increase was accompanied by the complete removal of all the majority traps and a reduction in the concentration of the minority traps (figure 8). This is interesting because, as shown in the following paper in this conference by S.R. Messenger et al., annealing treatments in the dark on electron irradiated MOCVD InP at temperatures in excess of 600 K does not remove all of the majority carrier signal. Illumination at 500 K for one hour is seen to further reduce the minority trap concentration and to cause more recovery in I_{sc}. V_{oc} was unaffected by the 500 K illumination. During a second 500 K annealing attempt, the cell failed.

Figure 9 shows the overall history of this cell. The results are dramatic. The thick line is the IV curve measured before irradiation. The irradiation up to 1×10^{16} 1 MeV electrons cm^{-2} is seen to almost destroy the cell. However,
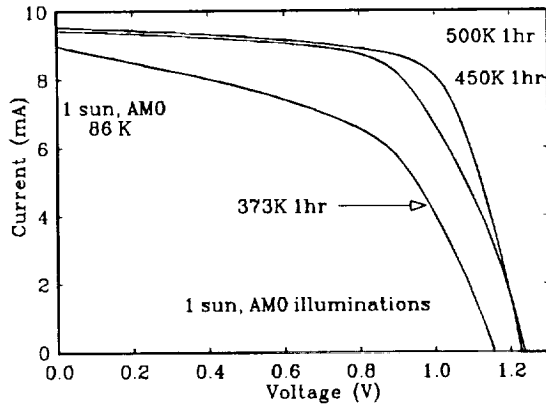
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Figure 7: The high temperature photo-injection annealing of an InP cell. The illumination at 450 K caused recovery in all of the PV parameters while annealing at 500 K only increased I_{sc}.
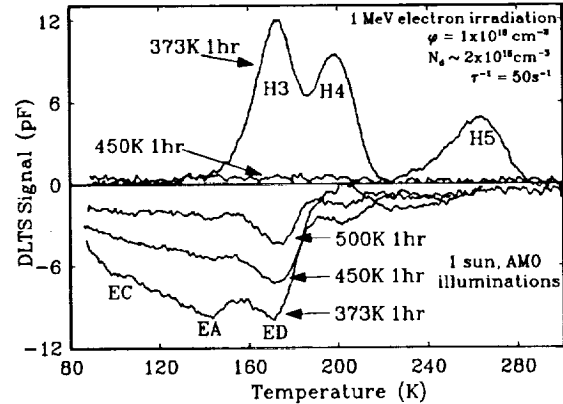
Figure 8: The annealing of the DLTS spectrum of the cell in figure 7. Illumination at 450 K removed all of the majority carrier traps. The 500 K illumination further reduced the minority carrier trap density.

the illuminations at increasingly higher temperatures cause significant recovery in the IV curves until after 1 hour at 450 K, the cell has achieved almost full recovery.
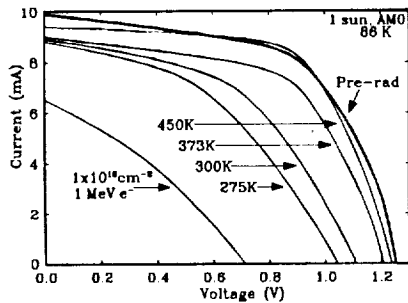
DISCUSSION

Figure 9: The full history of the annealing of the cell in figures 6-8. Even though the irradiation almost completely destroyed the cell, the illuminations caused almost full recovery.

The DLTS spectrum displayed in figure 1 is basically the same as that measured in irradiated MOCVD InP (ref 1,3,6,7); however, the minority carrier trapping centers in figure 1 are different than previously measured on thermally diffused InP (ref 3,6). While the activation energies given in table I of reference 3 may match those of the defects measured here (ref. 1,5,7), the positions of the negative peaks in the spectrum are different. More importantly, the annealing behavior of the minority carrier trapping centers reported by Yamaguchi et al. is entirely different than measured here and measured on the MOCVD samples (ref 3,6). Although, a full discussion of the implications of these differences is outside the scope of this paper, the point to be made is that the radiation-induced defect spectra in InP as they relate to solar cell performance are still not understood. Specifically, the minority carrier trapping centers, which this study has shown to affect the solar cell performance, have yet to be seriously investigated.

The results of the present annealing study clearly show that irradiated thermally diffused InP solar cells recover significantly when a current exists in the junction. The annealing occurs through a thermally activated process in which electron-hole pair recombination induces defect annealing which in turn induces recovery in the PV parameters. Furthermore, figures 1 and 2 seem to support the conclusion of Yamaguchi et al. that the H4 defect is the controlling factor (ref 3,6). However, the present study shows that this cannot be the entire story.

Considering equations 1 and 2, a recovery in I_{sc} indicates an increase in minority carrier lifetime (τ_n (assuming the depletion layer width does not change significantly). Since I_{sc} is recovering in figure 4, the implication is that the defect annealing brought on by the solar illumination causes recovery in the τ_n. Considering equation 3, V_{oc} is controlled by the junction dark current. InP has a band-gap of 1.34 eV, so the dark current is expected to be dominated by recombination. Therefore, since V_{oc} is observed not to recover, the suggestion is that the recombination current in the junction is not significantly changing. The strong correlation between the decrease in the H4 defect concentration (fig. 5) and the recovery of I_{sc} (fig. 4) suggests that the H4 defect acts to degrade τ_n. However, since the recombination current does not seem to be changing, H4 must not be acting as an efficient recombination center. Instead, it might be concluded that it is the H5 defect which increases the dark current and thus decreases V_{oc}. It is not unreasonable for H5 to be an efficient recombination center since it has an activation energy of 0.54 eV which is not far from mid-gap. Furthermore, McKeever et al. have shown that the H5 defect has a larger capture cross-section for minority than for majority charge carriers (ref 7). This is also supported by the data of figures 7 and 8 where V_{oc} is seen to almost completely recover at the same time that the H5 defect signal is removed.

$$L_n = \sqrt{D_n \times \tau_n}$$

$L_n \equiv$ *minority carrier diffusion length* (1)
$D_n \equiv$ *minority carrier diffusion coefficient*
$\tau_n \equiv$ *minority carrier lifetime*

$$I_{sc} \sim (W + L_n)$$

$W \equiv$ *depletion layer width* (2)

$$V_{oc} \sim \frac{kT}{q} \ln(\frac{I_{sc}}{I_o})$$

$k =$ *boltzmann's constant* (3)
$q =$ *the electronic charge*
$I_o =$ *junction dark current*

The data of figures 7 and 8 also support the correlation between the H4 defect and I_{sc}. When the H4 defect was completely removed, I_{sc} showed a large recovery. However, as seen in figure 9, the recovery is not complete. This may be due to the effect of the remaining minority carrier defect centers. The 1 hour anneal at 500 K caused the concentration of the minority carrier defects to decrease while I_{sc} increased but V_{oc} remained the same. This suggests that the electron traps are also acting to decrease τ_n. Since H4 has such a large introduction rate, it initially controls the solar cell output, but after H4 has significantly annealed, the effect of the minority traps becomes dominant. Furthermore, since the minority traps are the residual traps seen in the spectrum, they are expected to control the asymptotic limit on the recovery of the PV parameters. It is important to note that it is not known if longer illuminations at 500 K would induce further recovery. Thus, the ultimate limit on the cell recovery is yet to be determined.

Clearly, the radiation-induced degradation of thermally diffused InP solar cells anneals under solar illumination, and there are obvious trends in the DLTS spectra which link several of the defect levels to the particular annealing stages. Also, the measured defect spectrum shown in figure 1 is basically identical to that measured in MOCVD InP. However, irradiated MOCVD InP solar cells do not show this dramatic recovery under solar illumination (ref 1). This is quite puzzling and at present, no adequate explanation has presented itself.

CONCLUSIONS

The results of this research have clearly shown the radiation-induced degradation of thermally diffused InP solar cells to anneal under solar illumination. Therefore, under normal operating conditions, the InP cells would be expected to show virtually no degradation in a typical space radiation environment. Furthermore, apparent correlations between the recovery in the PV parameters and changes in the DLTS spectra have given significant insight into the mechanism by which these cells recover. The suggestion is that the H4 defect center acts to reduce τ_n which degrades I_{sc}. The minority carrier trapping centers were seen to also affect I_{sc}, presumably by also decreasing τ_n, and since the H4 defect anneals more rapidly than the electron traps, it is the electron traps which will set an upper limit on the cell recovery. The data also suggests that H4 does not act as a recombination center, but instead it may be the H5 defect which increases the dark current. This implies that it is the H5 defect, acting as an efficient recombination center, which causes a degradation of V_{oc}. It must be noted that since no direct measurements of the junction current (i.e. the dark IV curves) have yet been made, these conclusions are tentative. Nevertheless, these cells display an annealing property which makes them virtually insensitive to irradiation while in operation. With this property, InP technology is dramatically superior to Si and GaAs in a radiation environment. By exploiting the radiation resistance of InP solar cells, it will be possible to fly missions in severe radiation orbits which were previously inaccessible.

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