Solar Cells Active in Complete Darkness

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ABSTRACT: A graded bandgap multi-layer solar cell device structure was designed to absorb UV, visible and IR radiation, and to incorporate impact ionisation and impurity photovoltaic effects within one device. The design was experimentally tested with a well researched material system, MOVPE grown GaAs/AlGaAs. Open circuit voltages of ~1175 mV with highest possible FF values (0.83-0.87) and $J_{sc} \sim 12\ mAcm^{-2}$ have been observed [1,3]. These parameters were independently verified by measuring in five different laboratories in Europe and United States including NREL. While the work is continuing to increase short circuit current density values, these devices were tested to explore the experimental evidence of impurity PV effect, as expected from this design. Responsivity measurements and PV activity in dark conditions have been carried out to investigate impurity PV effect in these devices. Responsivity measurements indicate current collection in the infra-red region confirming the contribution from IR photons. The I-V measurements in dark conditions produce open circuit voltages exceeding 750 mV confirming the contribution from surrounding heat radiation. The new features of graded bandgap devices enable impurity PV effect to dominate and create useful charge carriers, suppressing detrimental recombination process. These experimental results will be presented in this paper.

Keywords: GaAs/AlGaAs, graded bandgap solar cells, impurity PV effect, thin film solar cells.

1 INTRODUCTION

Traditionally, solar radiation is exploited using two different methods; Infra-red (IR) radiation in "Solar Thermal Technology" and visible and ultra violet (UV) radiation in "Photovoltaic Technology". In order to be cost effective, it is attractive to combine both together in one device. In addition, if the incorporation of phenomena such as "impact ionisation" and "impurity photovoltaics" can be built into the same device, the performance of a solar cell can be enhanced. With these aims in mind, a graded bandgap multi-layer device structure has been designed and experimentally tested with well researched GaAs/AlGaAs system. This paper summarises the results obtained to date for graded bandgap solar cells, and the experimental evidence observed for the impurity photovoltaic effect in these device structures.

2 SUMMARY OF EXPERIMENTAL RESULTS

The device design proposed for combination of all above features is shown in Figure 1, and the details are published elsewhere [1-3]. The three most important steps for an efficient solar cell are satisfied for this structure according to solid state physics principles; namely (i) absorption of a major part of the solar spectrum, (ii) creation of e-h pairs in the presence of an internal electric field and (iii) effective separation of charge carriers towards two electrical contacts and transport through an external electric circuit. Because of the starting from a large bandgap p-type semiconductor and completing the device with a narrow bandgap n-type semiconductor, the probability of impact ionisation and the impurity PV effect has been increased. The detailed working of this device is illustrated with an animation placed in the website:

http://www.apsl.org.uk/dharme/default.aspx for readers use.

Figure 1. New design proposed for PV solar cells to maximise optical absorption, minimise thermalisation & transmission losses combining impurity photo-voltaics and impact ionisation.

The first attempt to grow this device structure was made using metal organic vapour phase epitaxy (MOVPE) - GaAs/AlGaAs materials. The growth started from an n-type GaAs substrate and the bandgap was gradually increased by increasing the aluminium content in the layers. The narrow bandgap end (back of the solar cell) was doped n-type with silicon (Si) and the
wide bandgap end (front of the solar cell) was doped p-type with background carbon (C) in the reactor. The thickness of the device was set to ~3.2 µm and Si-doping was gradually decreased towards the middle of the device. Then, the carbon incorporation was increased gradually by adjusting the growth temperature. This process was adopted expecting to create the device structure as shown in Figure 1, and the devices were fabricated by forming an ohmic contact to the GaAs substrate and a grid type contact to the front surface of the solar cell. Growth and processing details are given in one of our previous publications [2].

Different sizes of solar cells were fabricated as shown in Figure 2 for detailed characterisation of their PV activity.

![Figure 2](image)

**Figure 2.** Photograph of solar cells fabricated with different dimensions to test the effect of the scaling up process.

The current-voltage (I-V) curves under AM1.5 illumination were measured in five different laboratories for comparison, and to confirm accuracy of measurements. A typical I-V curve measured at NREL in USA is shown in Figure 3, and the detail results are summarised in Table I. It is clear that these devices produce \( V_{oc} \) values higher than the highest reported [4,5] to date, together with highest possible FF values in the mid 80%. However, \( J_{sc} \) values were low in the range (10-12) mA cm\(^{-2}\). Detailed studies carried out with electron beam induced current (EBIC) and secondary ion mass spectroscopy (SIMS) depth profiling showed that the first growth did not produced the expected device structure as shown in Figure 1. It was found that nearly flat band regions exist at both ends due to heavy doping of Si and C. Both Si and C doping has risen to \( \sim 10^{18} \) cm\(^{-3}\) levels towards the end of the solar cell during this first attempt.

![Figure 3](image)

**Figure 3.** A typical current-voltage curve measured under AM1.5 illumination for a (3×3) mm\(^2\) graded bandgap multilayer GaAs/AlGaAs solar cell showing \( V_{oc}=1171 \) mV, \( J_{sc}=12 \) mA cm\(^{-2}\), FF=0.85 and \( \eta\sim12\%\).

The second growth with reduced Si doping to achieve \( \sim 10^{15} \) cm\(^{-3}\), increased the depletion region at rear of the solar cell and the \( J_{sc} \) value rose to \( \sim 24 \) mA cm\(^{-2}\) as expected. But the reduction of C doping in the front of the device cannot be achieved using MOVPE technique. The work is continuing to grow the device structures using molecular beam epitaxy (MBE) technique in order to achieve these doping requirements.
Table I: Summary of solar cell parameters measured at five different laboratories for (3×3) mm² solar cells processed in one batch.

| Device | V_{oc} (mV) | FF | J_{sc} (mA cm⁻²) | R_{s} (Ω cm⁻²) | R_{p} (Ω cm⁻²) | Place of Assessment |
|--------|-------------|----|------------------|----------------|----------------|---------------------|
| 1      | 1170        | 0.87 | ---- | ---- | ---- | SHU Labs |
| 2      | 1160        | 0.86 | ---- | ---- | ---- | Dharmadasa et al |
| 3      | 1148        | 0.86 | 10.7 | 2.5 | 10,400 | Zürich Labs |
| 4      | 1141        | 0.86 | 10.3 | 4.0 | 5,100 | Tiwari et al |
| 5      | 1169        | 0.85 | 11.5 | ---- | ---- | SBU Labs |
| 6      | 1149        | 0.86 | 10.0 | ---- | ---- | Reehal et al |
| 7      | 1150        | 0.85 | 12.1 | 3.8 | ---- | EPFL Labs |
| 8      | 1159        | 0.85 | 12.3 | ---- | ---- | NREL - USA |
| 9      | 1171        | 0.85 | 12.0 | ---- | ---- | Emery et al |

3 SEARCH FOR EXPERIMENTAL EVIDENCE OF IMPURITY PV EFFECT

The device structure shown in Figure 1 was designed to incorporate impurity PV effect using high concentrations of defects naturally available closer to the GaAs substrate at the back of the device. The experiments were therefore performed in order to test the existence of this effect in these devices. The most relevant technique is the quantum efficiency (QE) measurement to test whether there is a collection of current in the infra-red region. The authors’ laboratory has no such facility to carry out these experiments. Therefore these devices were sent to several different laboratories equipped with this technique. There are two types of QE measurements which are used in solar cell assessments: external QE and internal QE. The external QE measurements include the effects of optical losses such as transmission through the cell and reflection from the surface. The internal QE refers to the efficiency with which photons that are not reflected or transmitted from the cell can generate collectable charge carriers. Internal QE is also referred to as incident photon to charge carrier efficiency (IPCE), and this is the method used to measure the cells produced in this project.

Figure 4 shows the IPCE measurements carried out for two devices in two different laboratories. Their features are similar, and the losses at UV and IR ends are due to high doping of the materials at both front and the back of the cell. These issues are dealt with separately in order to achieve full features shown in Figure 1 and increase the performance of the device structure. The aim of this work is to observe the impurity photovoltaic effect in these devices. All these IPCE measurements show a sharp cut-off at ~740 nm, and there is no collection in the IR region. According to these measurements, there is no contribution from the impurity PV effect in these devices.

Figure 4. Typical IPCE% curves measured for two (3×3) mm² solar cells. Note the sharp cut-off wavelength at ~740 nm indicating nil collection in the I-R region.

4 RESPONSIVITY MEASUREMENTS

The above measurements clearly raised an issue of disagreement between the theoretically expected impurity PV effect and the experimentally observed null results. This encouraged us to explore the ways of data collection, analysis and presentation of IPCE results and found that there are grey areas which are not clear to the experimentalists. For this reason, a simple measurement of responsivity as a function of wavelength was explored. Responsivity of a device is defined in the simplest way as
Responsivity (A/W) = Electrical output of the solar cell in (A)/Light input to the solar cell in (W).

This method is fully transparent to the experimentalist and removes all complications in data collection, analysis and graphical presentation. The devices were sent to measure responsivity against the wavelength to explore further.

Figure 5 shows a typical measurement and the main spectrum shows similar losses in UV and IR ends as observed in IPCE measurements. However, the collection in the IR region, from 800 - 1200 nm, is clearly observed in these measurements. This is a strong indication that during IPCE data collection, analysis and graphical presentations, this useful information is completely lost.

5 CURRENT-VOLTAGE (I-V) MEASUREMENTS UNDER DARK CONDITIONS

The positive indication of existence of impurity PV effect encouraged us to further investigate this effect using other techniques.

5.1 Current-voltage (I-V) as a function of light intensity

In order to test the behaviour of these devices, in diffused light the device parameters were measured as a function of light intensity. Table II summarises the device parameters observed under different illumination conditions. It is an excellent feature of this device that the \( V_{oc} \) and FF values saturate to their highest values even at 1% of the one-sun intensity, of 1.2 mW cm\(^{-2}\). In fact, this is almost dark, and the saturation of \( V_{oc} \) is a unique feature enabling the use of these devices in diffused light conditions. The production of \( V_{oc}=980 \text{ mV} \) and FF=0.81 at 1% of the one-sun intensity indicates that there is a positive contribution from IR radiation towards the PV activity of this device.

![Figure 5. A typical responsivity versus wavelength curve measured for graded bandgap devices. Note the positive response in the IR region up to ~1200 nm.]

Table II: Summary of device parameters observed for (3×3) mm\(^2\) solar cells, when measured individually and two cells connected in series, as a function of light intensity.

| Light Intensity (mW cm\(^{-2}\)) | \( V_{oc} \) (mV) | FF | \( J_{sc} \) (mA cm\(^{-2}\)) | \( V_{oc} \) (mV) | FF | \( J_{sc} \) (mA cm\(^{-2}\)) |
|-------------------------------|----------------|----|-----------------|----------------|----|-----------------|
| 1.2                           | 980           | 0.81| 0.10            | 1960           | 0.81| 0.12            |
| 10.5                          | 1080          | 0.83| 1.20            | 2160           | 0.83| 1.26            |
| 53.0                          | 1140          | 0.85| 6.19            | 2270           | 0.85| 6.49            |
| 100.0                         | 1150          | 0.85| 12.12           | 2310           | 0.85| 12.14           |

5.2 Current-voltage (I-V) measurements under complete darkness

The above observation of production of high values for \( V_{oc} \) and FF at lowest light intensity guided us to perform I-V characteristics under complete darkness and as a function of temperature. The devices were mounted inside a metal cryostat eliminating background light completely and the I-V characteristics were measured as a function of temperature. A typical set of linear-linear I-V curves observed under dark conditions are shown in Figure 6.
The observation of $J_{sc}$ and the production of $V_{oc}$ values in the region of (650 - 850) mV, under complete darkness confirms the PV activity created by thermal energy from the surrounding, and hence the existence of impurity PV activity in these devices.

In a separate I-V measurement system, diodes were measured under dark and illuminated conditions for further confirmation. Two such plots are shown in Figure 7, in both linear-linear and log-linear forms. Again the device exhibit ~1175 mV and ~950 mV open circuit voltage, under AM1.5 and in dark conditions respectively, re-confirming the activity due to IR radiation.

Figure 7. Linear-linear and log-linear I-V curves measured for graded bandgap devices under dark and AM1.5 illuminated conditions. Note the $V_{oc} \sim 950$ mV at complete darkness, and $V_{oc} \sim 1175$ mV under illumination.

6 DISCUSSION

The above observations highlight the existence of two power inputs to these graded bandgap multi-layer solar cells as shown in Figure 8; (i) the normal solar radiation when illuminated and (ii) the environment of the solar cell acting as an infinite heat reservoir. The heat from the surroundings also creates charge carriers in the device, especially at the back end and enhances the combined PV effect of the device. Production of charge carriers using I-R photons depends on naturally occurring defect levels specially occurring close to the growth substrate at the rear of the solar cell.

Table 11.2. Experimentally observed defect levels in MOVPE Al$_x$Ga$_{1-x}$As layers[6,7].

| Al content (x) | Activation Energy, $E_a$ (eV) | Approximate concentration (cm$^{-3}$) |
|----------------|--------------------------------|-------------------------------------|
| 0.05 - 0.11    | 0.41                           | $10^{13}$ - $10^{16}$               |
| 0.15           | 0.50                           | $10^9$                              |
| 0.20           | 0.55                           | $10^{15}$                           |
| (0.00 - 0.25)  | (0.80 - 0.90)                  | The varying EL2 level according to value of x |

The varying EL2 level according to value of x
It is appropriate to look at the deep energy levels present in MOVPE grown Al\textsubscript{x}Ga\textsubscript{1-x}As layers. This system is the most researched semiconductors next to silicon. The deep levels present are thoroughly studied and documented \cite{6,7} in the literature. Some of these are shown in Table III and therefore it is clear that there exists a ladder of deep levels in the bandgap. The concentration of these defects must be higher closer to the substrate. These levels therefore must be helping to create charge carriers using multi-step generation (or impurity PV effect), utilising IR radiation from surroundings.

The detrimental R\&G process also takes place in parallel, but the shape of this device allows impurity PV effect to dominate and positively contribute to overall PV effect. Therefore, when fully optimised, this device has a huge potential to increase $J_{sc}$ and hence the conversion efficiency.

7 CONCLUSIONS

The work presented in this paper leads to make several important conclusions.

(i) The responsivity measurements as a function of wavelength is simple, and experimentally confirms existence of impurity PV effect in graded bandgap multi-

![Figure 8](image)

Figure 8. Schematic diagram showing the two energy inputs available to this device structure. When placed in complete darkness, the device still produces PV activity using heat energy from the surrounding due to impurity PV effect.

layer devices. These observations are re-confirmed by the production of high $V_{oc}$ values together with other PV parameters in complete darkness. The theoretical expectation of existence of impurity PV effect is therefore experimentally confirmed for these new device structures.

(ii) The graded bandgap multi-layer solar cell structure has two power inputs; normal solar radiation and the surrounding heat energy. Heat energy creates charge carriers and this process will enhance the overall PV effect of the device when illuminated. Therefore when the doping concentrations are optimised to achieve fully depleted device, high $J_{sc}$ values and hence high efficiencies are expected from this device structure.

(iii) The current QE measurement systems miss-out some important information, most probably due to methods used for data collection, analysis and/or presentations of the results. This needs appropriate actions to improve this important PV characterisation technique.

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