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## **Spectral Characterisation of Photovoltaic Devices**

## Introduction to PV

**This technical note provides a comprehensive overview of current photovoltaic (PV) devices and the spectral characterisation techniques used in the evaluation of their efficacy in the goal of harnessing a maximum of energy from the sun and artificial sources of light.**

### Overview

PV devices exploit the photovoltaic effect, first discovered by Becquerel in 1839, to generate a voltage and current under exposure to light. The history of the practical PV device however, does not begin until 1954 where Bell Laboratories demonstrated a silicon solar cell with a modest conversion efficiency of six per cent. The subsequent development of solar cells as the major energy source for satellites in orbit started 4 years later with Vanguard.

The extra-terrestrial application of PV devices acted as a catalyst for a flurry of rapid advances in the field. Today, PV IN SPACE remains the driving force behind breakthroughs in the industry, progressing in parallel with the use of PV devices as a renewable energy source and consumer devices, albeit with differing terms of reference.

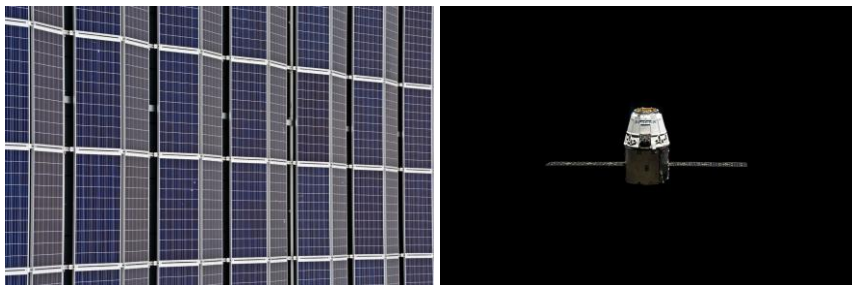
Whilst high budget space applications place more of an accent on energy production efficiency, with cost a secondary consideration, the use of PV for renewable energy and consumer products is very much focused on cost reduction.

Despite the typically significant cost associated with manufacturing and installing PV devices, the energy generated is essentially free, and widely available. Due to this, solar energy is now considered the most a viable renewable source for global energy requirements, alongside for use in consumer devices.

### PV Device Materials

PV device types are generally classified in three generations.

The first generation devices, adopting the technological advances of the microelectronics industry, are based on single-junction crystalline silicon which currently remains the most common material for PV devices.



High efficiency devices result from the quality material used, yet at the cost of expensive manufacturing techniques. Furthermore, due to relatively poor light absorption, devices need to be several hundred microns thick, representing a significant raw material cost.

As a push for cheaper PV devices is encountered, recourse is being made to second generation devices, which benefit from thin-film technology.

Since these materials have good light absorption, up to a factor 100 less material is required, an immediate material saving results. In addition to this, process techniques are much less complex and therefore cheaper, and, significantly in some instances, can be processed at low

temperatures opening up the possibility of creating devices based on a flexible plastic substrate.

Nothing is free, however. These devices are also characterised by a poorer material quality which results in the loss of light-generated electrons to defects in the structure, and a corresponding reduction in efficiency.

Third generation devices encompass a vast panoply of technologies, aimed at improving the efficiency of existing devices, or introducing different materials and material structures.

These include multiple junction devices, combining materials responding to different spectral regions, mirror/lensbased concentrators to increase the level of light exposure of the device, up to the equivalent of hundreds of suns and organic polymer and dye-sensitised devices, based on very low cost technology and available on flexible substrates.



### Light Conversion Processes

The operation of a PV cell requires the absorption of light to generate either an electron-hole pair or exciton and the separation of charge carriers to an external circuit.

In a semiconductor pn junction, an incident photon of the correct wavelength (and therefore energy) excites an electron from the valence band to the conduction band, leaving behind a hole. An in-built voltage across the pn junction sweeps away these carriers to an external circuit before they can re-combine.

A similar process is at play in organic cells, whereby light incident on the organic layer excites an electron to the lowest unoccupied molecular orbit (LUMO) leaving behind a hole in the highest occupied molecular orbit (HOMO). The electronic properties of either the electrodes or a heterojunction are tailored to separate the charge carriers, to be passed to an external circuit.

The situation in a dye-sensitised solar cell, composed of a dye, an oxide layer (commonly TiO<sub>2</sub>) and an electrolyte redox system, is rather different. An electron in the dye is excited by incident light, and transferred to the conduction band of the TiO<sub>2</sub> layer and then to the external circuit. The dye takes an electron from the electrolyte through a process of oxidation. The oxidised electrolyte diffuses to the counter electrode where electrons are re-introduced having flown through the external circuit.

### Impact Upon Test Methods

These very different physical processes have an interesting consequence in the measurement of spectral response where measurements with a monochromatic probe should be performed under simultaneous illumination by a solar simulator. To discriminate between the

photocurrent generated by the solar simulator from that generated by the monochromatic probe, the latter is modulated with the use of an optical chopper.

Since carrier transport in semiconductors and organic PV devices is very fast compared with dyesensitised devices, it follows that in the latter case very low chopping frequencies or CW operation of the monochromatic probe is necessary.

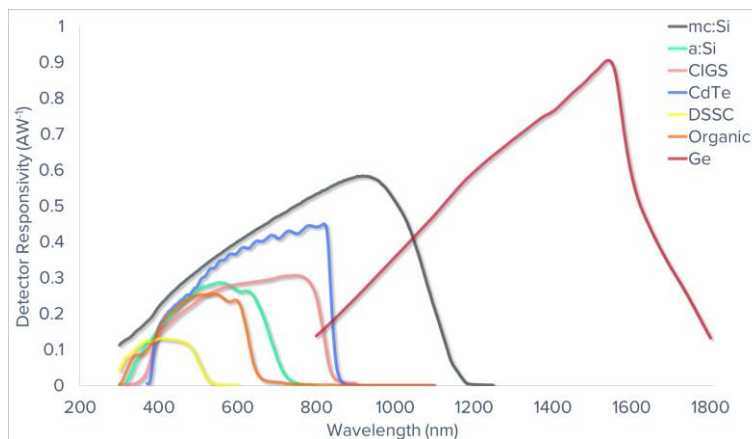
### Source Spectrum

Whether the illuminating source be the sun or artificial light, it is clearly desirable to obtain PV devices that both respond to as much of the broad source emission range as possible and have a maximum responsivity, or conversion efficiency.

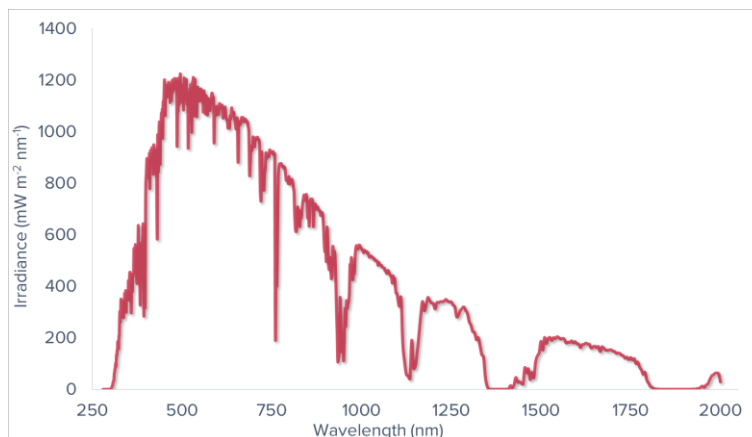
In practice, devices respond only to a restricted range of wavelengths, as illustrated below, limited at long wavelengths by the material band gap, and at short wavelengths by material absorption.

Device spectral response depends upon a large number of factors, including material system, device design, electrical contact etc. and for single junction pn devices is limited by the Shockley– Queisser limit.

The combination of these parameters may be evaluated in considering the device energy conversion efficiency.



Spectral responsivity of a selection of current PV devices, to be compared with the AM1.5G reference spectrum

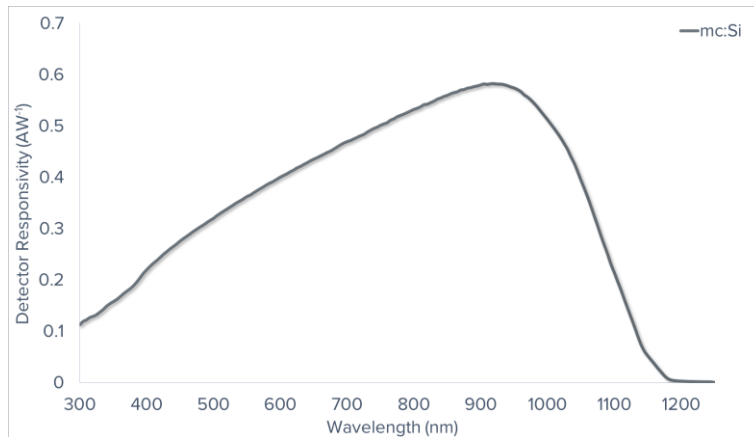


## Measurement Quantities

Along with an I-V measurement, the following quantities provide the most information of material and PV device function.

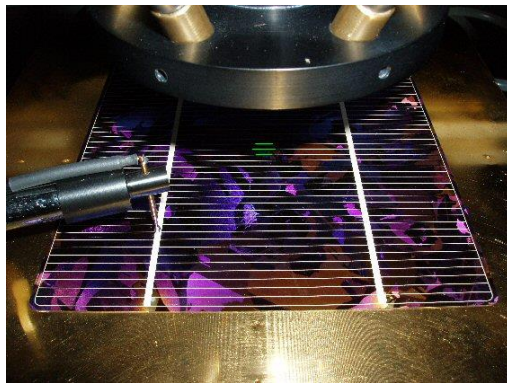
### Spectral response

The spectral response ( $A W^{-1}$ ) of a PV device provides information on the physics at play in the global device, taking into account not only the material, but also the reflectance and transmittance of the device.



Spectral response of Silicon solar cell

This measurement is performed by shining a monochromatic probe beam onto the sample and registering the photocurrent generated as a function of wavelength.



Care should be taken to ensure the probe beam is not shaded by electrical connections, or that the shading is taken into account by correcting the resulting response.

The probe is first characterised, using a detector of known responsivity ( $A W^{-1}$ ) to determine the power in the beam. Subsequent measurement of the photocurrent generated by the device under test as a function of wavelength allows for the determination of spectral responsivity.

The conditions under which this measurement should be performed is discussed overleaf.

### External Quantum Efficiency (IPCE)

The external quantum efficiency (EQE) is defined as the number of electrons provided to the external circuit per photon incident on the device, and is directly obtained from the spectral response measurement by the following argument.

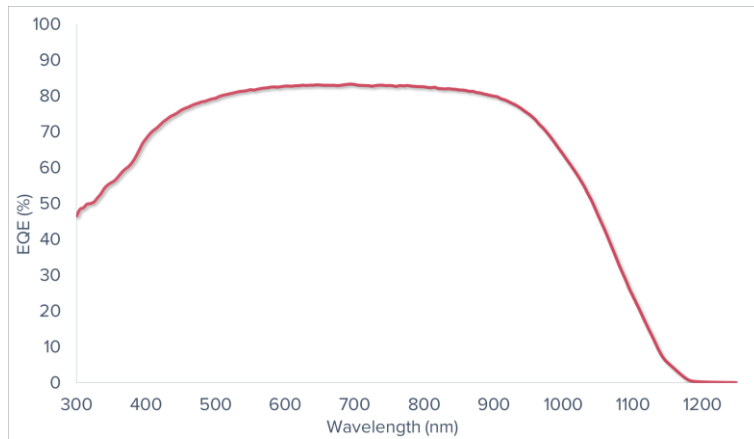
The number,  $n$ , of electrons generated by the device,  $n=(It/e)$ , where  $I$  is the generated current,  $t$  time and  $e$  the charge of the electron.

The number,  $m$ , of photons, incident on the sample,  $m= Pt/ E_v$ , where  $P$  is the power in the beam,  $t$  time, and  $E_v$  the photon energy. The quantum efficiency,  $\eta$ , is defined as,

$$\eta = 100.n/m = 100.(It/e)/(Pt/E_v) = 100.(I/P).(E_v/e)$$

$$\Rightarrow \eta = 100.S.(hc/e).(1/\lambda) \approx 1239.84.S/\lambda (\%)$$

Where  $S$  is the spectral responsivity in  $A.W^{-1}$  and  $\lambda$  the wavelength in nm. EQE can therefore be determined directly from a measurement of the spectral response.



EQE response of Silicon solar cell

### Calculation of $J_{sc}$

The measured spectral response may be used to predict the expected device short circuit current density,  $J_{sc}$ , under standard testing conditions. This is simply calculated by evaluating the following integral over the spectral range of response of the device under test.

$$J_{sc} = \int S_t(\lambda).E_0(\lambda).d\lambda$$

Where  $J_{sc}$  is in  $A.m^{-2}$ ,  $S_t(\lambda)$  is the device spectral response, in  $A.W^{-1}.nm^{-1}$  and  $E_0(\lambda)$  the AM1.5 reference spectrum in  $W.m^{-2}.nm^{-1}$ .

### Spectral Mismatch

I-V measurements of PV devices, used to determine amongst other things the device  $J_{sc}$  and  $I_{sc}$ , should be performed under AM1.5 illumination.

A reference cell is often used to determine the irradiance of the solar simulator used. Where the spectral response of the reference cell differs from the test cell, the mismatch factor should be computed from:-

$$M = \frac{\int E(\lambda).S_t(\lambda).d\lambda}{\int E_0(\lambda).S_t(\lambda).d\lambda} \cdot \frac{\int E_0(\lambda).S_r(\lambda).d\lambda}{\int E(\lambda).S_r(\lambda).d\lambda}$$

Where  $S_r(\lambda)$  is the reference device spectral response,  $S_t(\lambda)$  the test device spectral response,  $E_0(\lambda)$  the AM1.5 reference spectral distribution, and  $E(\lambda)$  the solar simulator spectral distribution. Since these parameters appear in both numerator and denominator, normalised

quantities may be used.

Where required, the irradiance of the solar simulator should be set to:-

$$G_{set} = \frac{G_{ref}}{M}$$

Where  $G_{ref}$  is the reference irradiance of  $1000 \text{ W.m}^{-2}$

### Reflectance and Transmittance

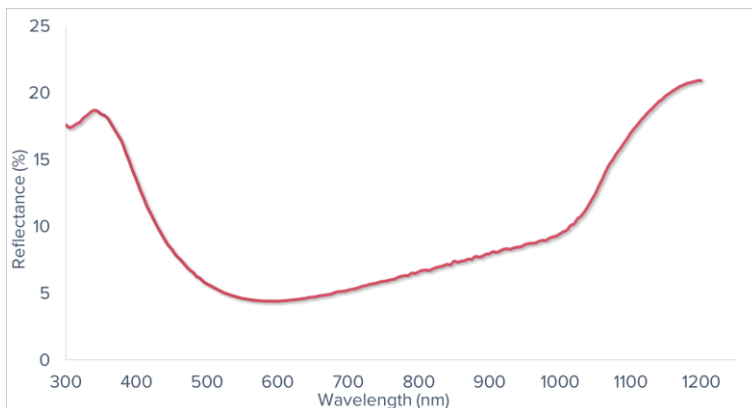
In an ideal world, all photons reaching a PV device are transmitted only to the active region where the conversion process occurs.

Due to the refractive index of the materials used, light shall be reflected from the front surface of the device (to mitigate which anti-reflection coatings are applied). In the case of thin-film devices one should also consider that light may be transmitted through the sample.

The total reflectance (diffuse and specular), and the total transmittance (diffuse and normal), of the device can be measured with the aid of an integrating sphere.



In addition to providing a manner of determining device IQE (below), these measurements also permit the characterisation of anti-reflection coatings and the transmission of thin film layers.



Reflectance of Silicon solar cell

### Internal Quantum Efficiency

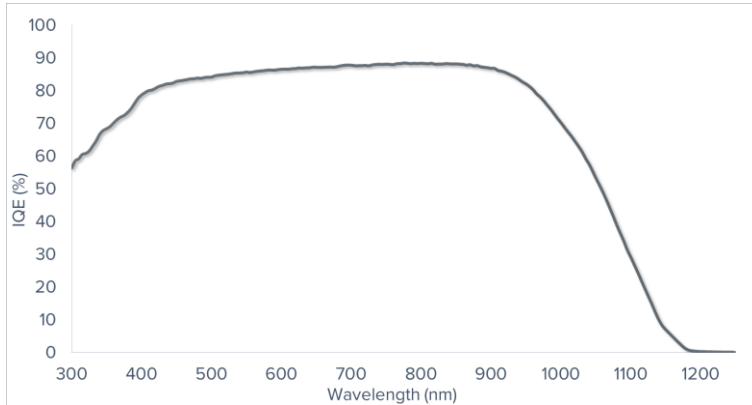
Based on the above measurements of reflectance and transmittance, the EQE can be modified to take into account only the portion of the incident light reaching the active region, to yield the internal quantum efficiency.

This allows a better understanding of the material properties of the device.

Internal quantum efficiency is simply expressed as:

$$IQE = EQE / (1 - R - T)$$

Where R is the reflectance, and T the transmittance of the sample.

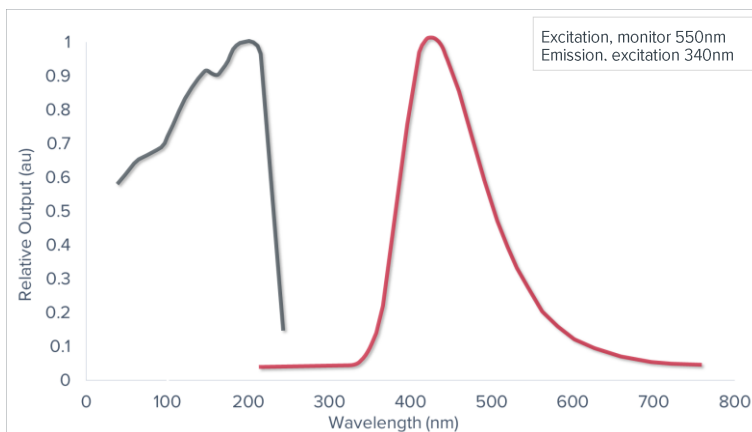


Internal quantum efficiency of Silicon solar cell

### Luminescent Material Characterisation

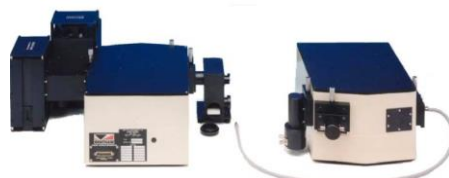
The physical process of luminescence may be harnessed in two instances.

1. The efficiency of PV devices may be enhanced significantly by down-shifting and up-converting non-absorbable photons, to produce photons having an energy better matching the device spectral response.
2. Fluorescent solar collectors are composed of a mixture of fluorescent dyes embedded in a transparent medium. Absorbed incident sunlight is re-emitted at longer wavelengths and transported to the edge of the collector by total internal reflection, where a solar cell is located.



Excitation and emission measurement

The characterisation of such materials requires a dual monochromator system, including an excitation and an emission monochromator. The two monochromators may be used together to investigate material excitation and emission properties.



Fluoro300 highly configurable fluorometer utilised in the high-accuracy assessment of both solid and liquid samples



## Standard Testing Conditions

In order to perform measurements of spectral response/ EQE (IPCE) in a consistent manner, transferable between laboratories, standard testing conditions are essential. Indeed, in the case of certain PV technologies, measurement is possible only under very specific conditions.

### Overview

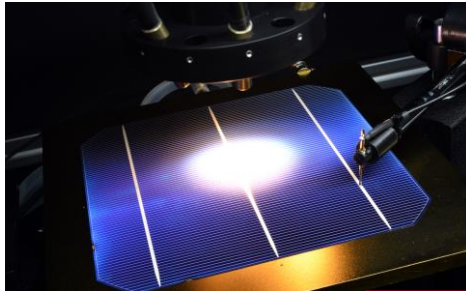
The measurement of spectral response/ EQE (IPCE) International standards are published to provide guidelines for the testing required of photovoltaic devices, for example IEC 60904-1 describes I-V testing, IEC 60904-3 the determination of module efficiency, IEC 60904-8 single junction device relative spectral response measurements and ASTM E2236 multi-junction spectral response measurements.

In essence, these standards specify the conditions of the measurements of PV devices requiring, for example, the use of a solar simulator approximating AM1.5G at an irradiance of  $1000 \text{ Wm}^{-2}$ , and controlled sample temperature.

One must also give consideration to certain specific technologies or cell architectures which will admit to testing only under very specific conditions.

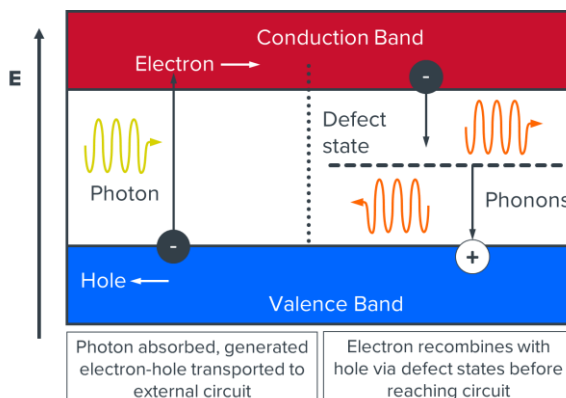
### Solar Simulator

The use of the solar simulator physically places the device in true operating conditions, and is related particularly to material quality.



In poorer quality material, where the crystal structure is defective, there are traps and defects to which generated carriers are lost, leading to incorrectly reported spectral response.

Light from the solar simulator generates a large number of carriers in the material which can pump defects and traps, ensuring that the carriers generated by the probe beam are not thus lost, compared to measurements with the probe without solar bias.



Indeed, the use of solar simulators in the case of monolithic multi-junction (MJ) devices is essential as discussed overleaf.

### Voltage Biasing

Spectral response / EQE measurements are usually performed under short circuit conditions. In the case of multi-junction solar cells however, the voltage over non-tested junctions can result in the junction under test operating in reverse bias, which situation is not desired, especially where the subcell has a low reverse breakdown voltage.

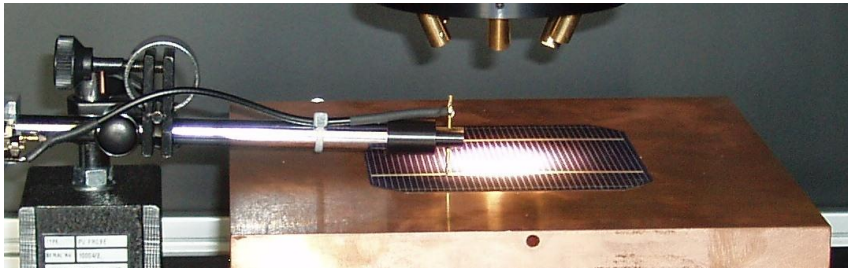
In the case of thin-film solar cells, the spectral response/ EQE may be voltage dependent. Defects in the material leads to a reliance on the electric field in the space charge region for minority carrier collection, leading therefore to a dependence on the device operating voltage.

### Temperature Control

Sample temperature control is also an important consideration since as sample temperature rises, the properties of the devices are modified (one obtains with device heating a red shift in the response), and its efficiency can decrease as more energy is lost to phonons in the lattice.

A means of countering the heating effect attendant to exposure to the light bias should be employed at all times.

Furthermore, it may be beneficial to explore the temperature dependence of PV technology to evaluate more accurately device operation in the field.



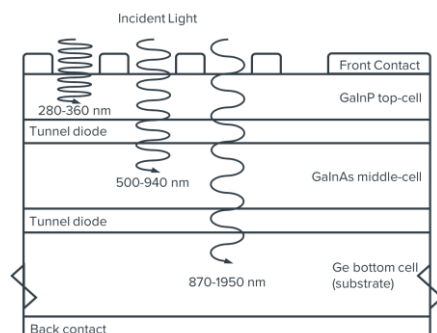
## Multi-Junction Requirements

Whilst standards<sup>1</sup> exist for the evaluation of the spectral response of monolithic multiple junction (MJ) solar cells, the measurement procedure is far from standard.

Without such guidance, however, it is likely that in the case of subcells having low shunt resistance or low reverse breakdown voltage, significant measurement errors will result.<sup>2</sup>

### Introduction

In seeking to measure the spectral response/EQE of monolithic MJ solar cells, such as the III-V monolithic GaInP/GaInAs/Ge triple junction solar cell depicted here, the measurement of component subcells on an individual basis is not possible since they are epitaxially grown on one substrate and interconnected by tunnel diodes.



<sup>1</sup> ASTM- E2236-05 "Standard Test Methods for Measurement of Electrical Performance and Spectral Response of Nonconcentrator Multijunction Photovoltaic Cells and Modules"  
<sup>2</sup> Meusel et al, "Spectral Response Measurements of Monolithic GaInP/Ga(In)As/Ge Triple-Junction Solar Cells: Measurement Artifacts and their Explanation", Prog. Photovolt: Res. Appl. 2003; 11:499-514

Subcell spectral response must therefore be determined by making use of the effect of current limitation, achieved through light biasing.

### Light Biasing

In addition to biasing the subcell under test at a level of one sun to simulate use conditions, it is necessary to light bias the non-tested subcells at a higher intensity such that the former generates the smallest photocurrent and is therefore current limiting. It follows that good control of the light bias source spectrum is required.

### Subcell Interactions

Since the current of the MJ cell is limited by the subcell under test, it follows that the non-tested cells with excess photocurrent operate close to their  $V_{oc}$ . If the MJ cell is tested under short circuit conditions, then a negative voltage approximately equal to the sum of the  $V_{oc}$  of the other cells is placed across the tested subcell.

Whilst the photocurrent generated by light biasing may be considered as a constant, the presence of the monochromatic probe gives rise to changes in subcell operating voltage, depending on the probe wavelength and the response range of the current limiting subcell under test.

Where the subcell under test has nonideal properties such as a low shunt resistance or a low reverse breakdown voltage, often exhibited in low bandgap materials such as germanium, this can lead to changes in the measured photocurrent, and the incorrect reporting of spectral response/EQE: the outcome depends largely on the true nature of the I-V curves of both the subcell under test and that of the nontested subcells.

Outside the response range of the subcell under test, the monochromatic probe gives rise to an increase in operating voltage of the non-tested cells, compensated for by a reduction in the operating voltage of the subcell under test. This may give rise to an increase in  $J_{sc}$ , showing a response where one is not expected. Within the subcell response range, the presence of the monochromatic probe will directly lead to an increase in  $J_{sc}$ , shifting the non-tested cells to lower operating voltage, and compensated by an increase in the voltage of the tested subcell. The resulting current may be less than that expected in response to the monochromatic probe, leading to a lower reported spectral response/EQE. Both effects are commonly observed phenomenon in the measuring the bottom cell of the GaInP/GaInAs/Ge triple junction solar cell.

### Voltage Biasing

Shifting the external voltage of the cell will tend to minimise both of the above effects: in moving to higher gradient regions of the I-V curve of the nontested cells, lower shifts in subcell operating voltage are encountered, giving rise to less variation in the current of the cell under test.



### Optimisation of Light Biasing

Increasing the photocurrent generated by the non-tested subcells leads to increased gradient of the I-V curve in the proximity of their operating voltage, whilst reducing the photocurrent generated by the subcell under test will lead to a reduction of operating voltage closer to  $V_{oc}$  where the gradient of the I-V curve is steepest.

Both will give rise to less variation in the current of the cell under test, and is achieved through appropriate filtering.



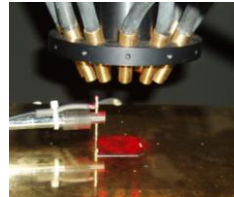
## MJ Cell Example

For the correct measurement of the GaInP/GaInAs/Ge triple junction solar cell, the following procedure is recommended.

Current limiting may be verified by spectral response measurement at various levels of non-tested cell light bias intensity.

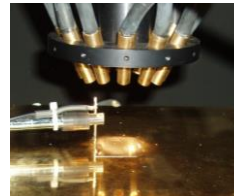
### GaInP top junction

The GaInP junction responds ~300-700nm. The device under test should be illuminated simultaneously by a solar simulator at one sun bias, and a second simulator filtered with a red long-pass filter. The spectral response may then be measured directly over the extended range 300-800nm.



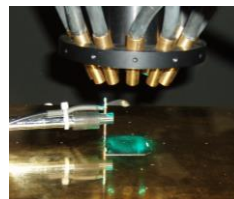
### GaInAs middle junction

The GaInAs junction responds ~500-900nm. The device under test should be illuminated simultaneously by a solar simulator at one sun bias, and a second simulator filtered with a blue band pass filter, transmitting also in the infra red. The spectral response may then be measured directly over the extended range 300-1100nm.

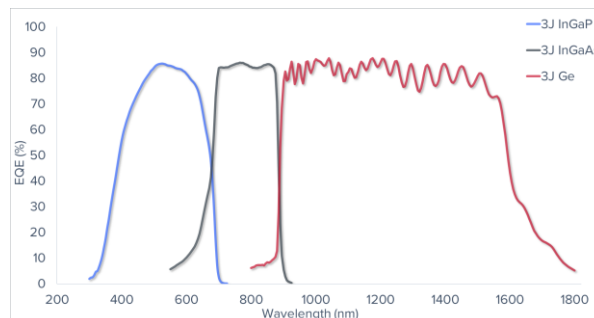


### Ge bottom junction

The Ge junction responds ~900-1800nm. The device under test should be illuminated simultaneously by a solar simulator at one sun bias, and a second simulator filtered with an IR rejection filter. To take this subcell to short circuit condition, an external voltage should be applied. Under dual solar simulator irradiation, the operating voltage,  $V_{op}$  of the top two junctions is recorded (typically ~2-2.5V). The voltage across the device should then be set to  $-V_{op}$  to take the third junction into short circuit.



The spectral response may then be measured directly over the extended range 800-1800nm. Where the correct bias voltage is used, a maximum spectral response should be recorded. This may be verified by repeating the measurement at other levels of voltage bias.



External quantum efficiency of InGaP, InGaAs and Ge three junction solar cell