Introduction to Organic Solar Cell Devices & Electrical Characterization

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Introduction

• Conventional solar cell devices are essentially based on inorganic materials, Silicon (Si) occupying the lead. Si technology is well established, with solar cells having efficiency over 20% for single junction devices.

Fig.1.1: Example of high-efficiency Si Heterojunction Solar cell device

• Even though these devices have high conversion efficiencies and are quite stable (over 20 years), they however have some drawbacks:
  ○ High fabrication cost, associated with infrastructural requirement, cleanroom, etc.
  ○ Energy intensive processes (foundries, etc.)
  ○ Shortage of Si, as it is also used in micro-electronics

These shortfalls have made the photo-voltaic industry to consider other solar cell technologies such as organic solar cell devices.

• An organic solar cell device or organic photovoltaic cell (OPVC) is a class of solar cell that uses conductive organic polymers or small organic molecules for light absorption and charge transport. These devices are relatively easy to fabricate, can also be processed on flexible substrates, however they have relatively low conversion efficiencies and offer low stability.
Fig: 1.2 Example of Organic solar cell device

- Organic materials commonly used in OPVC include:
  - Poly(3-hexylthiophene) (P3HT) – electron donor, hole-transport material
  - [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) – electron acceptor, a fullerene derivative
  - Poly(3,4-ethylenedioxythiophene) : Poly(styrenesulphonate) (PEDOT:PSS) – hole transport (electron blocking) layer

During the laboratory session will be fabricating a typical OPVC having the following layers:
- ITO on glass substrate (PDMS ?): rf sputtering
- Organic Layers by spin coating
  - PEDOT:PSS
  - P3HT:PCBM
  - Al electrode back contact by evaporation

Each layer will be characterized (four-point probe, surface profiler, XRD including grazing incidence, SEM, UV-VIS spect) and finally the whole device will be characterized making use a solar simulator.

**Some Properties of Organic Semiconductors**
- One of the main differences is that photoexcitation in organic materials
does not automatically lead to the generation of free charge carriers, but to bound electron-hole pairs (excitons) with a binding energy of about 0.4eV

- These excitons need to be split up (or dissociate) before the charges can be transported through the film and collected at the electrodes. For example, exciton dissociation can occur at a rectify

Energy band diagram

- The energy levels in molecular materials can be related to the energy levels of inorganic semiconductors:
  - The energy needed to release an electron from the valence band of an inorganic semiconductor to the vacuum level is the ionisation potential, while the electron affinity is the energy gained when an electron is transferred from the vacuum level to the conduction band edge.

Fig. 1.3: Simplified Energy band diagram of a Semiconductor

- In molecular materials also electrons can be liberated from the highest occupied molecular orbital (HOMO) to the vacuum. The energy involved can roughly be estimated on basis of the electrochemical oxidation potential (vs. NHE) of the molecules using the relation: \( E_{HOMO} \approx E_{NHE} - V_{ox} \), with \( E_{NHE} = -4.5 \text{ V vs. vac.} \)
- In a similar way the electron affinity can be estimated from the reduction potential of the molecules using: \( E_{LUMO} \approx E_{NHE} - V_{red} \). The difference
between both energy levels corresponds to the **optical bandgap** of the molecules.

- The concentration of mobile charge carriers within intrinsic molecular layers in the dark at room temperature is usually small. The resulting conductivity of these layers is therefore relatively small.
- Intentional doping to form n- or p-type layers is not straightforward, since this causes often degradation of the organic material.

![Energy band diagram of an Inorganic Semiconductor and a Molecular Semiconductor](image)

**Fig. 1.4:** Energy band diagram of an Inorganic Semiconductor and a Molecular Semiconductor

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### Some Organic Solar Cell Device Architectures

OPV devices are found in different device configurations such as single layer, bilayer, blend, laminated layers, etc. In the section, we shall explore the above configurations, highlighting their limitations.
Single Layer Devices

- **Single layer organic solar cell** is made up of an organic layer sandwiched between two electrodes:
  - The front electrode is a thin transparent layer of metal or Transparent conducting oxide (TCO) such as Indium Tin oxide (ITO); It is imperative this layer should have a high work function.
  - The back electrode is a metal with a relatively low work function. Al, Mg, Ca, are commonly used.

![Single Layer Organic Solar cell](image)

Fig. 1.5 Single Layer Organic Solar cell

- Once an external circuit is made by connecting the two electrodes with a conductor, the difference in the work functions creates an electric field in the organic layer

- If we recall that upon absorption of light, the electrons are excited to the LUMO leaving hole in the HOMO, forming excitons, the electric field in the organic layer will therefore help to break up the exciton pairs, pulling electrons to the positive electrode and holes to the negative electrode

- Single layer organic solar cells are also referred to as Schottky diode since the rectification occurs at only one interface (organic layer / metal electrode), the other electrode forming an ohmic contact with the organic semiconductor.

- This class of solar cell though simple to fabricate has low quantum efficiency and conversion efficiency. The drawback is due to the fact that the electric field (in the organic layer) resulting from the difference in work functions of the two electrode is usually not sufficient to achieve an effective separation of the exciton pairs.
• There is rather an electron-hole recombination process in the organic layer. Furthermore, in the single layer device both the electrons and the holes travel in the same material and recombination losses are generally high.

### Double Layer (Bilayer) Devices

- The **double layer organic solar cell** improves the functionality of the single layer OPV by including a distinct organic Donor layer and a distinct Acceptor layer between the two previous electrodes.

- These two layers of materials have differences in electron affinity and ionization energy, therefore electrostatic forces are generated at the interface between the two layers. The materials are chosen properly to make the differences large enough, so these local electric fields are strong, which may break up the excitons much more efficiently than the single layer photovoltaic cells do.

- The layer with higher electron affinity and ionization potential is the **electron acceptor**, and the other layer is the **electron donor**.

![Bi-layer Organic Solar Cell Device](image)

**Fig. 1.6:** Bi-layer Organic Solar Cell Device

- The Bi-layer structure is also called **planar donor-acceptor heterojunctions** solar cell device.

- The drawback is the small interface that allows only excitons of a thin layer to reach it and get dissociated.

- A typical polymer layer needs a thickness of at least 100 nm to absorb enough light. At such a large thickness, only a small fraction of the excitons can reach the
heterojunction interface, bearing in mind that the diffusion length of excitons is on the order of 4-10 nm

## Blend Layer (or Bulk Heterojunction) Devices

- Instead of having distinct donor and distinct acceptor layers, in the blend layer solar cell device, the electron donor and acceptor are mixed together, forming a polymer blend.

- If the length scale of the blend is similar with the exciton diffusion length, most of the excitons generated in either material may reach the interface, where excitons break efficiently. Electrons move to the acceptor domains then were carried through the device and collected by one electrode, and holes were pulled in the opposite direction and collected at the other side. The strong point of this type is the large interface area if the molecular mixing occurs on a scale that allows good contact between alike molecules (charge percolation) and most excitons to reach the D/A interface.

- This type of configuration is also called a dispersed heterojunction organic solar cell device.

![Blend Organic Solar Cell Device](image)

**Fig. 1.7: Blend Organic Solar Cell Device**

## Laminated Layer Devices

- This relatively recent type represents the successful attempt to unify the advantages of the two structures above. Laminated polymer donor-acceptor device may be considered as an intermediate of the bilayer and the blend device.

- Charge separation occurs in the blend layer in the middle that is obtained after
laminating the two separate layers together and charge transport can only occur via the correct transport layer. This structure also features the useful options to treat each layer separately (e.g. doping, physical/chemical conversion) before forming the blend layer and instant encapsulation between the two substrates. The drawback is that certain mechanical properties of the organic semiconductors are required (low glass transition temperature) to form the intermixed layer.

Fig. 1.8: Laminated Layer Organic solar cell device

**Operations of Organic Solar Cell**

Fig. 1.9: Operations of an Inorganic solar cell
• For an inorganic solar cell, when photons from the sun hit a cell, they are absorbed and create electron-hole pairs. The electrons and holes are attracted to electrodes at opposite surfaces of the semiconductor, creating a potential difference, and electricity can be generated. This is however different for OPVC.

![Image of an organic solar cell process]

**Fig. 1.10: Processes occurring in an organic solar cell**

• A photon is absorbed in the polymer, thus creating an exciton.

• The nascent exciton dissociates into separated charge carriers. This process is facilitated by the presence of an electron acceptor, which accepts the electron while the hole remains on the polymer chains.

• The difference in work functions of the electrodes gives rise to an electric field which drives the separated charge carriers towards electrodes.

• The charge carriers are collected at the electrodes. If an electrical circuit is connected to the electrodes, an electrical current flows through it.

• In general, for a successful organic photovoltaic cell five important processes have to be optimized to obtain a high conversion efficiency of solar energy into electrical energy:
  - *Absorption of light and generation of excitons*: The absorption spectrum of the photoactive organic layer should match the solar emission spectrum and the layer should be sufficiently thick to absorb most of the incident light.
  - *Diffusion of excitons to an active interface*: Ideally, all excitons should reach the
photo-active interface within the exciton lifetime ($\tau_{\text{EXC}}$), since the excitons diffusion length is about 10nm, only those excitons formed within a distance of 10nm from the interface will contribute to charge separation.

- **Charge separation:** In most organic solar cells, charges are created by photoinduced electron transfer. In this process an electron is transferred from an electron donor (D) material to an electron acceptor (A) material with the aid of the additional input energy of an absorbed photon with energy $h\nu$.

- **Charge transport:** After the charge transfer the electrons and holes are in close proximity and therefore there is a large chemical potential gradient that drives the charge carriers away from the exciton dissociating interface.

- **Charge collection:** This is generally accomplished by a transparent conductive oxide (TCO) such as ITO or SnO$_2$:F on one side and a metal contact such as Al on the other side.

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**Fig. 1.11:** Schematic drawing of the working principle of an organic photovoltaic cell.

Illumination of a donor material (in red) through a transparent electrode (ITO) results in the formation of an exciton (1). Subsequently, the exciton is transported by diffusion (2) to the interface between the donor material and an acceptor material (in blue). Electron is transferred to the acceptor material (A$^-$), leaving a hole at the donor material (D$^+$) (3). The photogenerated charged carriers are then transported (4) to and collected at opposite electrodes (5). A similar charge generation process can occur, when the acceptor is photoexcited instead of the donor.
Solar Cell Characteristics

Photovoltaic (PV) Cell Circuit model

![Solar Cell Equivalent Circuit](image)

**Fig 1.12 Solar Cell Equivalent Circuit**

- The series resistance ($r_s$) represents the ohmic losses at the front contact, impurity concentration, and junction depth. It reduces the short-circuit current ($I_{sc}$) and consequently the maximum output power ($P_{max}$).

- The shunt resistance ($r_{sh}$) represents the loss due to diode leakage current (crystal defects, etc.)

Current-voltage Characteristics

- In the dark, the I-V characteristics (*dark I-V*) of the solar cell are similar to those of a diode.

- Under illumination (by making use of a solar simulator), the following I-V curve is obtained for a typical PV cell.
The important parameters of the cells under illumination are:
- The short-circuit current $I_{sc}$
- The open circuit voltage $V_{oc}$
- The maximum power point $P_{max}$
- The Fill Factor (FF) is given by
  \[ FF = \frac{P_{max}}{I_{sc} V_{oc}} = \frac{I_{max} V_{max}}{I_{sc} V_{oc}} \]
  \( FF \) is a measure of how squarable the output of the PV cell is.
- The Conversion Efficiency of the cell is expressed as
  \[ \eta = \frac{P_{max}}{P_{in}} \]
  where $P_{max}$ is the maximum power extracted from the cell
  $P_{in}$ is the total radiant energy incident on the surface of the cell

**Degradation of OPVC**
- Unfortunately OPVs currently have very short lifetimes. There are several possibilities for mechanism of degradation:
  - Environmental and intrinsic factors
  - Light (photodegradation)
  - Temperature, humidity, presence of oxygen
- Chemical composition, morphology
- Can be physical or chemical degradation

Fig. 1.14: Degradation mechanisms in OPVC
2. ORGANIC SOLAR CELL DEVICE FABRICATION

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Introduction

- The organic solar cell device is essentially a multi-layer system, the layers required are generally
  - A transparent conducting oxide (TCO) such as Indium Tin Oxide (ITO), usually deposited by sputtering
  - Organic layers deposited either by spin coating or thermal vacuum evaporation
  - Metal electrode such as Al deposited by thermal vacuum evaporation

Sputtering of Transparent Conducting Layer (TCO)

- Sputtering is a physical process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions.
- The sputtered atoms, since they are not in their thermodynamic equilibrium state, tend to condense back into the solid phase upon colliding with the substrate, kept a few cm above the target.
- Argon is generally used to create an Ar⁺ plasma.

Fig. 2.1: Schematic of Sputtering process
• The steps involved in the sputtering process are:

  ◦ The substrates are cleaned and mounted in the vacuum chamber

  ◦ The vacuum chamber is initially evacuated (pumped down) to a relatively high-vacuum level (< 2X10^{-5} Torr), making use of a vacuum rotary pump (mechanical pump) and a high vacuum pump such as diffusion pump or turbo-molecular pump

  ◦ The sputtering gas such as Argon is admitted into the chamber in the controlled manner making use of a mass flow controller; this brings the chamber pressure to about 10^{-3} Torr

  ◦ An rf generator (13.56MHz) supplies the desired rf power to the system (across the target and the substrates). A plasma is therefore created and the sputtering process begins

  ◦ A pre-sputtering phase of about 10min is normally recommended to clean the target before opening the shutter, thereby exposing the substrate.

  ◦ The thickness is monitored using a thickness monitor. Once the desired thickness is reached, the shutter is closed, the rf generator is turned OFF, the sputtering gas supply is also closed.

  ◦ The chamber is vented to Nitrogen gas and the samples removed from the chamber.

  ◦ For some materials, there is need to either heat up the substrate during the sputtering process or carry out a post annealing step at a desired temperature.

• Typical process parameters for ITO sputtering are:

  ◦ Rf power: 50W
- Ar flow rate: 2 sccm
- Substrate temperature: 250°C

![Edwards Auto 306 Sputtering System](image)

**Fig.2.2:** Edwards Auto 306 Sputtering System

**Organic layer deposition: Spin coating**

- There are four distinct stages in the spin coating process:
  - Deposition of the coating fluid onto the wafer or substrate: This can be done by using a nozzle and pouring the coating solution or by spraying it onto the surface. Spin coaters usually have 2 modes of dispense: (i) static dispense (solution dispensed on a steady substrate), and (ii) dynamic dispense (solution dispensed while the substrate is rotating at a slow speed)
  - Acceleration of the substrate up to its final, desired, rotation speed
  - Spinning of the substrate at a constant rate; fluid viscous forces dominate the fluid thinning behavior
Spinning of the substrate at a constant rate; solvent evaporation dominates the coating thinning behavior.

Back Electrode Deposition: Thermal Vacuum Evaporation

• In an thermal vacuum evaporation system, the material (to be evaporated) is heated up to its boiling point by applying the desired electric current to a resistive heater (crucible or filament).

• The material therefore evaporates and condenses on the surface of the substrate.

• Thermal vacuum evaporation is essentially used for metallization.

Fig.2.3: Spin-coater
Fig. 2.4: Edwards Auto 306 Thermal Vacuum Evaporator
3. ORGANIC SOLAR CELL DEVICE ELECTRICAL CHARACTERIZATION

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Introduction

The electrical characteristics are essentially:

- The sheet resistance for the thin film or the bulk
- The Current-voltage (I-V) curve for the complete devices

The Four-Point Probe Resistivity Measurement Technique

The Four-Point Probe is a technique usually used to measure sheet resistance of a bulk material and a layer thin film. The instrument can also be used for the determination of film thickness. If the film thickness is known (for instance using the step height determination function of a surface profiler), then the resistivity (consequently the conductivity) of the layer can be computed.

- The probe head contains 4 equally spaced pins, in-line or at the corner of a square. The pins are brought into intimate contact with the surface of the thin film or wafer to be characterised. Note here that it is imperative that the probes and the film should make an ohmic contact (and not a Schottky barrier junction).

- A Source-Measure Unit (SMU) allows a fixed current to flow through the 2 outer pins, and the voltage is measured across the 2 inner pins (for the in-line configuration).
Four-Point Probe Theory

**Bulk Material** (*probe spacing* \( s << t \) *sample thickness*)

For a bulk sample, where the probe spacing \( s \) is negligence before the sample thickness, the current flow from the outer probes follow spherical paths.

The bulk resistivity \( \rho \) in this case is given by

\[
\rho = 2\pi s \frac{V}{I}
\]

**Assignment 1**

*Derive the expression of bulk resistivity for the case of bulk sample*

**Thin Layer** (*probe spacing* \( s >> t \) *sample thickness*)

For thin layers such as thin films, the film thickness \( s \) is negligible before the probe spacing. In this case, the current flow emanating from the 2 outer probes can be assumed to follow circular paths. The sheet resistivity in this case is expressed as

\[
\rho = \frac{\pi t}{\ln 2} \left| \frac{V}{I} \right|
\]

The above expression does not depend on the probe spacing, but rather on the film...
thickness. The sheet resistance $R_s$ can now be obtained as $R_s = \frac{D}{t}$

$$R_s = \frac{\pi}{\ln 2} \left( \frac{V}{I} \right)$$

The quantity $\pi/\ln 2$ is called the geometric factor $k$. For a layer a thin film and in the case of in-line probe head configuration, $k = 4.53$

**Assignment 2**

*Derive the expression of the sheet resistance for a layer of thin film*

**Current-voltage Voltage Measurement**

In the laboratory, once a device (such as p-n junction diode, solar cell, etc.) is fabricated, there is always a need to investigate its response when it is forward and reversed biased.

- Care should be taken to avoid interfering with the measurements, especially when measuring very small currents (order of pA).

- It is equally important to avoid damaging the device under test (DUT) by allow to much current to flow through the DUT.

**I-V Setup**

There are usually different measurement approaches. Let us consider the following 2 circuits :

**Circuit 1**
In the above circuit, the resistance, $r$, limits the current flowing through the DUT, to avoid damaging it

In this case, the current $I$ flowing through the DUT is accurately measured

There is always a potential drop across the measurement tool (Ammeter), and consequently the value of the voltage across the DUT ($V_{DUT}$) as measure by the voltmeter is not exact.

To minimize the above error it is important to ensure that the impedance of the Ammeter ($Z_A$) is negligible before the impedance of the DUT ($Z_{DUT}$)

**Exercise**

Assuming the extreme case where the impedance of the ammeter $Z_A$ is of the same order of magnitude with that of the DUT (for example $Z_A = Z_{DUT}$), evaluate $V_{DUT}$, conclude on the accuracy of the measurement.
Circuit 2

- The voltage across the DUT ($V_{DUT}$) is accurately measured.

- There is also a current flowing through the voltmeter (due to its internal resistance, it provides a path to the flow of current), the current as recorded by the ammeter is actually the sum of the current flowing through the DUT ($I_{DUT}$) and that of the current flowing through the voltmeter (undesired). Therefore the reading of the Ammeter is not the true representation of the intended current to be measured.

- In this case, it is imperative that the impedance of the voltmeter ($Z_v$) should be very large compared to that of the DUT ($Z_{DUT}$).

- This second case is generally used for device characterization since it yields a better accuracy. It also called the 4-wire measurement set-up where two wires from the SMU source the current through the DUT while the other 2 wires sense the voltage directly across the DUT, minimizing therefore the errors due the impedance of the lead wires.
Exercise

Assuming the extreme case where the impedance of the voltmeter $Z_V$ is of the same order of magnitude with that of the DUT (for example $Z_A = Z_{DUT}$), evaluate $I_{DUT}$, conclude on the accuracy of the measurement.
p-n Junction Diode Characteristics

For an ideal p-n junction diode, the I-V characteristics follow the following equations:

**Forward Bias**

\[ I_f = I_0 \left( e^{\frac{qV_{appl}}{nk_BT}} - 1 \right) \]

where the reverse saturation current \( I_0 \) is defined as

\[ I_0 = n_i^2 q A \left( \frac{1}{N_A} \sqrt{D_p} + \frac{1}{N_D} \sqrt{D_n} \right) \]

where \( D_p \) and \( D_n \) are the hole and electron diffusion constants respectively, \( \tau_p \) and \( \tau_n \) are the minority carriers lifetime

The variable \( n \) is the ideality factor
Fig. 3.2  p-n Diode
For most diodes, the basic characterization is the DC diode parametric test (or Functional Test). These tests are:

- Forward Voltage Test ($V_F$)
- Leakage current Test ($I_L$)
- Reverse Breakdown Voltage Test ($V_R$)

### Forward Voltage Test ($V_F$)

The Forward Voltage Test involves sourcing a positive bias current and sensing the potential drop across the diode. There is an initial large increase of potential drop across the junction as the current starts to increase, but subsequently, the voltage quickly saturates and becomes almost constant if the current is increased further.
Reverse Breakdown Voltage Test ($V_R$)

The Reverse Breakdown Voltage test is conducted by applying a negative (reverse) bias current to the diode while sensing the voltage drop across the junction. $V_R$ is achieved when any increase in current only results in a small increase in voltage. Values of $V_R$ are in the order of tens of volts, depending on the diodes.

Reverse Leakage Current ($I_L$) Test

For the measurement of the leakage current, a Reverse bias voltage less than the reverse breakdown voltage is applied across the diode and the Reverse Leakage Current is measured. The Reverse Leakage Current Test is a bit difficult, since it involves a very low current. A special test fixture constructed with high resistance materials and an appropriate guarding technique (as illustrated below) are usually required to reduce leakage currents in test fixture and cables, and therefore ensure an acceptable test.
Fig. 3.5 Guarding technique to reduce leakage current during low current measurements
LED Characteristic

LED testing is similar to the diode testing where the forward voltage test, the leakage current and the reverse breakdown voltage are evaluated. However, besides the electrical characterization, it also involves and optical characterization.

**Forward Voltage (VF) Test**

The LED conducts when it is in forward bias. There is an initial large increase of potential drop across the junction as the current starts to increase, but subsequently, the voltage quickly saturates if the current is increased further. The LED normally operates in this early region where $V$ is almost constant.

Similar to the p-n diode, the Forward Voltage test is carried out by using a SMU to source current and measure the resulting voltage drop across the device. Typical current values are in the range of milliamps to some amps while the measured voltage is in the order of some volts.

The LED chromaticity and the amount of light emitted during the forward voltage test are closely related to the current flowing through the LED. By placing a photodetector close to the LED or by placing the LED in an integrating sphere, the optical characterization can be carried out.

**Reverse Breakdown Voltage ($V_R$) Test**

The Reverse Breakdown Voltage test is conducted by applying a negative (reverse) bias current to the LED while sensing the voltage. $V_R$ is achieved when increase in current only results in small increase in voltage. Values of $V_R$ are in the order of tens of volts.

**Reverse Leakage Current ($I_L$) Test**

For the measurement of the leakage current, a Reverse bias voltage less than the reverse breakdown voltage is applied across the LED and the Reverse Leakage Current is measured.
Photovoltaic (PV) Cell Characteristics

**Fig 3.6  Solar Cell Equivalent Circuit**

- The series resistance ($r_s$) represents the ohmic losses at the front contact, impurity concentration, and junction depth. It reduces the short-circuit current ($I_{sc}$) and consequently the maximum output power ($P_{max}$).

- The shunt resistance ($r_{sh}$) represents the loss due to diode leakage current (crystal defects, etc.).

A typical setup for the electrical characterization (light and dark) of a PV is...
In the dark, the I-V characteristics (dark I-V) of the solar cell are similar to those of a diode.

Under illumination (by making use of a solar simulator), for the light I-V measurement, the source-measure unit is programmed to source a voltage from 0V, and measure the current flowing in the cell, the process continues until the current becomes 0 A. The following I-V curve is obtained for a typical PV cell
The important parameters of the cells under illumination are:

- The short-circuit current $I_{sc}$
- The open circuit voltage $V_{oc}$
- The maximum power point $P_{max}$

- The Fill Factor (FF) is given by

$$FF = \frac{P_{max}}{I_{sc} V_{oc}} = \frac{I_{max} V_{max}}{I_{sc} V_{oc}}$$

$FF$ is a measure of how squarable the output of the PV cell is.

- The Conversion Efficiency of the cell is expressed as

$$\eta = \frac{P_{max}}{P_{in}}$$

where $P_{max}$ is the maximum power extracted from the cell

$P_{in}$ is the total radiant energy incident on the surface of the cell.