2

SEMICONDUCTORS AND P-N JUNCTIONS

2.1 SEMICONDUCTORS

In 1839 Becquerel observed that certain materials, when exposed to light, produced an electric current (Becquerel, 1839). This is now known as the photovoltaic effect, and is the basis of the operation of photovoltaic or solar cells.

Solar cells are manufactured from semiconductor material, that is, material which acts as an insulator at low temperatures, but as a conductor when energy or heat is available. At present most solar cells are silicon based, since this is the most mature technology. However, other materials are under active investigation and may supersede silicon in the long term.

The electrical properties of semiconductors can be explained using two models, the "Bond" and the "Band" models. These models are described briefly below. (More detailed descriptions are given in Green, 1992 and Neville, 1978].

2.1.1 The Bond Model

The bond model uses the covalent bonds joining the Si atoms to describe semiconductor behaviour. Figure 2.1 illustrates the bonding and the movement of electrons in a silicon crystal lattice.
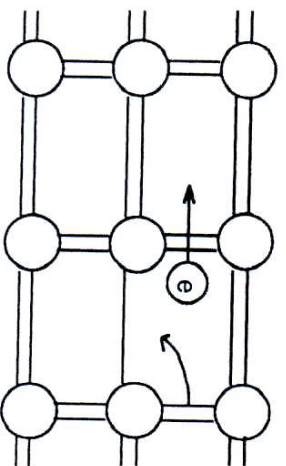
Figure 2.1: Schematic representation of covalent bonds in a silicon crystal lattice.

At low temperatures the bonds are intact and the silicon behaves as an insulator. At high temperatures, some bonds are broken and conduction can occur by two processes:

electrons from broken bonds are free to move; and electrons from neighbouring bonds can also move into the "hole" created in the broken bond, allowing the broken bond or hole, to propagate as if it had a positive charge.

The concept of a moving "hole" is analogous to that of a bubble in a liquid. Although it is actually the liquid that moves, it is easier to describe the motion of the bubble going in the opposite direction.

2.1.2 The Band Model

The band model describes semiconductor behaviour in terms of the energy levels between valence and conduction bands. This is illustrated in Figure 2.2.
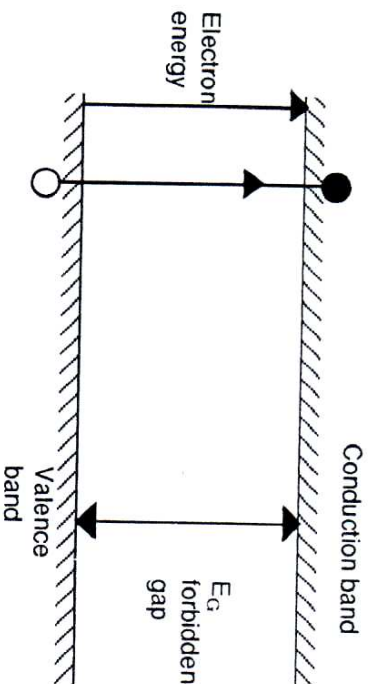

Figure 2.2: Schematic of the energy bands for electrons in a solid.

The electrons in covalent bonds have energies corresponding to those in the *valence band*. In the *conduction band* the electrons are free. The *forbidden band gap* corresponds to the energy needed to release an electron from a covalent bond to the conducting band where it can conduct a current. The *holes* remaining conduct in the opposite direction in the valence band, as described for the bond model.

2.1.3 Doping

It is possible to shift the balance of electrons and holes in a silicon crystal lattice by "doping" it with other atoms. Atoms with one more valence electron than silicon are used to produce "n-type" semiconductor material. Atoms with one less valence electron result in "p-type" material. This is illustrated in Figure 2.3.
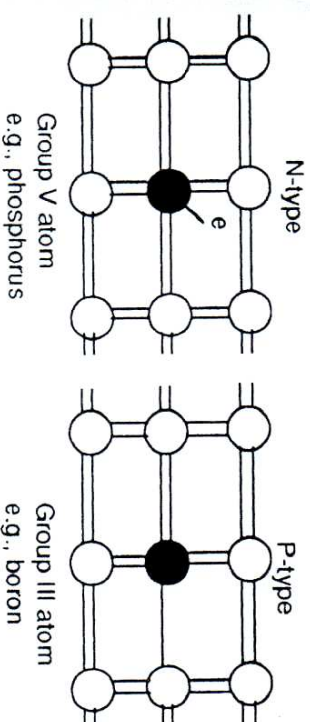

Figure 2.3: Schematic of a silicon crystal lattice doped with impurities to produce n-type and p-type semiconductor material.

2.2 SEMICONDUCTOR TYPES

Silicon, or other semiconductor material, used for solar cells can be crystalline, multicrystalline, polycrystalline or amorphous. The structure of the different material types is illustrated in Figure 2.4.

2.2.1 Crystalline Silicon

Crystalline silicon has an ordered crystal structure, with each atom ideally lying in a pre-ordained position. It therefore allows ready application of the theories and techniques developed for crystalline material, described in previous sections, and exhibits predictable and uniform behaviour. It is, however, the most expensive type of silicon, because of the careful and slow manufacturing processes required. The cheaper multicrystalline or polycrystalline silicon (poly-silicon), and amorphous silicon are therefore increasingly being used for solar cells, despite their less ideal qualities.

2.2.2 Polycrystalline Silicon

The techniques for production of multi- or poly-crystalline silicon are less critical, and hence cheaper, than those required for single crystal material. The grain boundaries reduce the cell performance by blocking carrier flows, allowing extra energy levels in the forbidden gap, thereby providing effective recombination sites, and providing shunting paths for current flow across the p-n junction.

crystalline
(c-Si)

multicrystalline or polycrystalline (poly-Si) - regions of crystalline Si separated by "grain boundaries" where bonding is irregular

amorphous (a-Si:H) - like a liquid, with less regular arrangement of atoms leading to internal "dangling bonds"
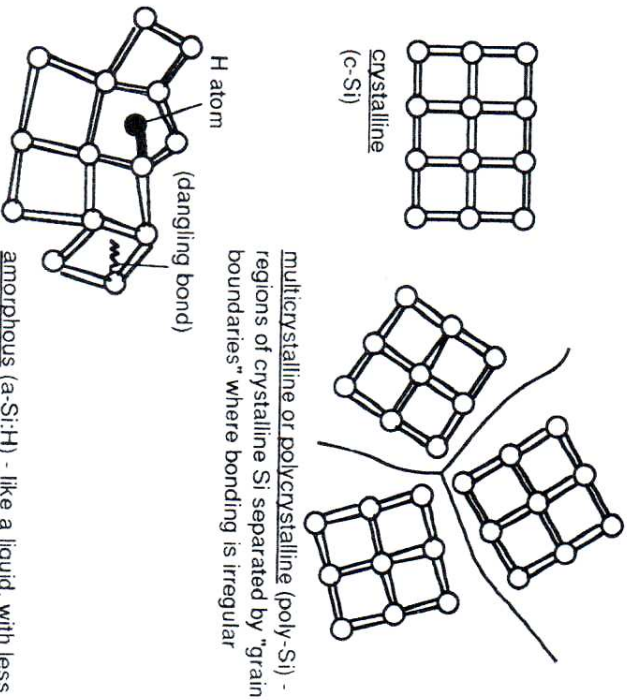
H atom

(dangling bond)

Figure 2.4: The structure of crystalline, multicrystalline, polycrystalline and amorphous silicon (multicrystalline silicon differs from polycrystalline silicon only in the size of the crystalline regions between "grain boundaries").

To avoid significant recombination losses at grain boundaries, grain sizes in the order of a few millimetres are required (Card & Yang, 1977). This also allows single grains to extend from front to back of the cell, providing less resistance to carrier flow and generally decreasing the length of grain boundaries per unit of cell. Such multicrystalline material is widely used for commercial solar cell production.

2.2.3 Amorphous Silicon

Amorphous silicon can be produced, in principle, even more cheaply than poly-silicon. There is no long-range order in the structural arrangement of the atoms, resulting in areas within the material containing unsatisfied, or "dangling" bonds. These in turn result in extra energy levels within the forbidden gap, making it impossible to dope the semiconductor when pure, or to obtain reasonable current flows in a solar cell configuration.

It has been found that the incorporation of atomic hydrogen in amorphous silicon, to a level of 5-10%, saturates the dangling bonds and improves the quality of the material. It also increases the band gap, E_g, from 1.1 eV in crystalline silicon to 1.7 eV and is much more strongly absorbing for photons of energy above the latter threshold. The thickness of material required to form a functioning solar cell is therefore much smaller.

The minority carrier diffusion lengths in such silicon-hydrogen alloys, (a-Si:H), are much less than 1 μm. The depletion region therefore forms most of the active carrier collecting volume of the cell. Different design approaches to those discussed above for crystalline silicon are therefore used. In particular, as large a "depletion region" as possible is created. Figure 2.5 illustrates the general design of an a-Si:H solar cell.

P

undoped (intrinsic I)
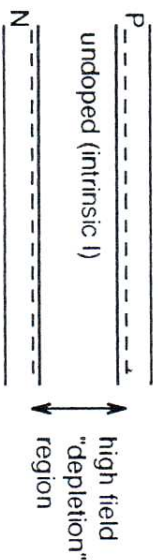
N

high field "depletion" region

Figure 2.5: Schematic of an a-Si:H solar cell

A-Si and other "thin film" technologies for solar cell manufacture, where films of very thin semiconductor are deposited onto glass or other substrates, are used in many small consumer products, such as calculators, watches and "non-critical" outdoor applications. In principle, thin films provide a very low cost means of cell production. However, to date, performance and lifetimes are not high enough to warrant large scale use. Research into thin film and other potentially low cost solar cell materials aims to see these dominating the market over coming decades.

2.3 ABSORPTION OF LIGHT

When light falls onto semiconductor material, photons with energy E_{ph}, less than the band gap energy E_G interact only weakly with the semiconductor, passing through it as if it were transparent.

However, photons with energy $E_{ph} > E_G$ interact with electrons in covalent bonds, using up their energy to break bonds and create "electron-hole" pairs which can then wander off independently. This is illustrated in Figure 2.6.
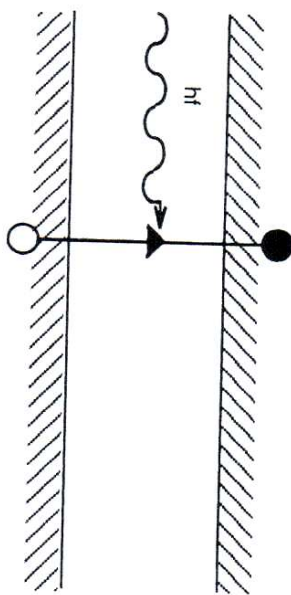

Figure 2.6: The creation of electron-hole pairs when illuminated with light $E_{ph} = hf$, where $E_{ph} > E_G$.

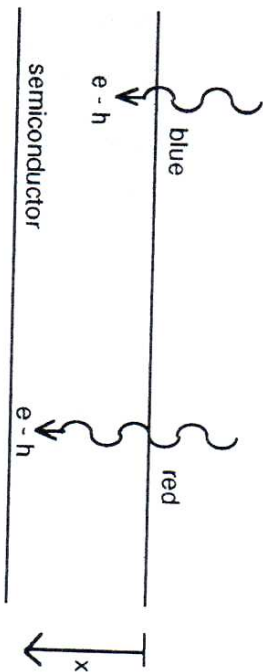The higher the photon energy, the more quickly the light is absorbed, as illustrated in Figure 2.7.

Figure 2.7: The light energy dependency of electron-hole generation.

The generation rate G of electron-hole (e-h) pairs per unit volume can be calculated using the formula:

$$G = \alpha N e^{-\alpha x} \tag{2.1}$$

where: N = photon flux (photons/unit area/sec.), α = absorption coefficient, and x = distance before absorption. The value of α as a function of the wavelength of light is illustrated in Figure 2.8 for silicon at 300K.

2.4 RECOMBINATION

When the light is switched off, the system must return to a state of equilibrium and the electron-hole pairs generated by the light must disappear. With no external source of energy, the electrons and holes wander around until they meet up and recombine. Any defects or impurities within or at the surface of the semiconductor promote recombination.
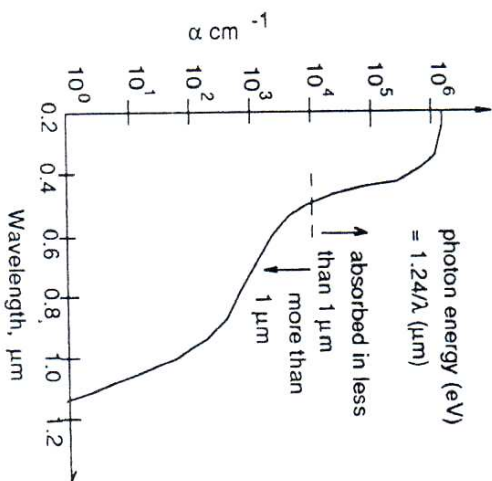

Figure 2.8: The absorption coefficient, α, in silicon at 300K as a function of the vacuum wavelength of light.

The carrier lifetime of a material is defined as the average time for recombination to occur after electron-hole generation. For silicon this is typically 1 μs. Similarly, the carrier diffusion length is the average distance a carrier can move from point of generation until it recombines. For silicon this is typically 100-300 μm. These two parameters give an indication of material quality and suitability for solar cell use. However, no power can be produced from a semiconductor without a means of giving directionality to the moving electrons. Therefore, functional solar cells are typically produced from semiconductor material by the addition of a rectifying p-n junction.

2.5 P-N JUNCTIONS

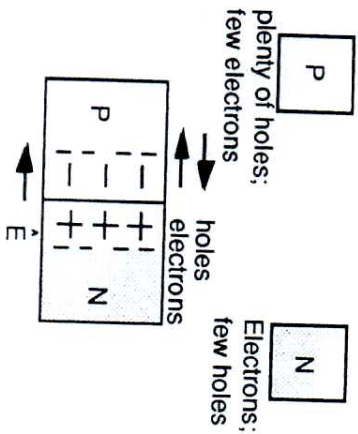P-n junctions are formed by joining n-type and p-type semiconductor materials, as shown in Figure 2.9.

When joined, the excess holes in the p-type material flow by diffusion to the n-type, while electrons flow by diffusion from n-type to p-type as a result of the carrier concentration gradients across the junction. They leave behind exposed charges on dopant atom sites, fixed in the crystal lattice. An electric field Ê therefore builds up in the so-called "depletion region" around the junction to stop the flow. Depending on the materials used, a "built in" potential V_{bi} due to Ê will be formed. If a voltage is applied to the junction, as shown in Figure 2.10, Ê will be reduced.

plenty of holes; few electrons

Electrons; few holes

holes electrons

Figure 2.9: Formation of a p-n junction.
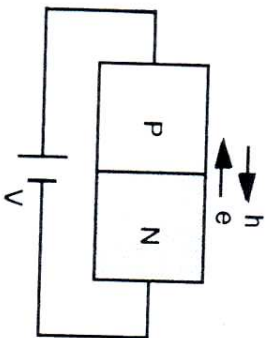

Figure 2.10: Application of a voltage to a p-n junction.

Once Ê is no longer large enough to stop the flow of electrons and holes, a current is produced. The "built in" potential reduces to (V_{bi} - V) and the current flow increases exponentially with the applied voltage. This phenomenon results in the *Ideal Diode Law*, expressed as:

$$I = I_o [\exp(qV/kT) - 1] \tag{2.2}$$

where:

I_o	=	"dark saturation current", the diode leakage current density in the absence of light
V	=	applied voltage
q	=	absolute value of electronic charge
k	=	Boltzmann's constant
T	=	absolute temperature

Note that:

I_o increases as T increases

I_o decreases as material quality increases.

At 300K, $kT/q = 25.85$ mV, the "thermal voltage"

For actual diodes, the expression becomes:

$$I = I_o[\exp(qV/nkT) - 1] \tag{2.3}$$

where:

n = ideality factor, a number between 1 and 2 which typically increases as the current decreases.

The diode law is illustrated for silicon in Figure 2.11.

Si
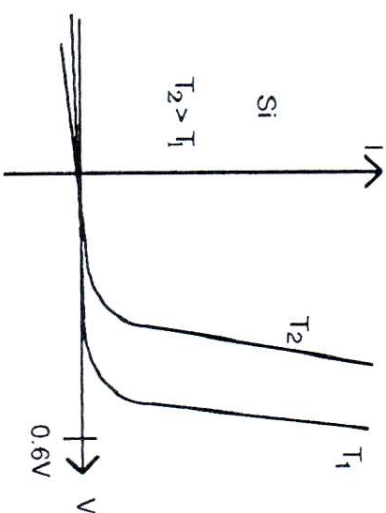
$T_2 > T_1$

T_2

T_1

0.6V

V

I

Figure 2.11: The diode law for silicon - current changes with voltage and temperature. For a given current, the curve shifts by approximately 2 mV/°C.

EXERCISES

2.1. The absorption coefficient of silicon decreases from 1.65 x 10^6/cm at 0.3 μm wavelength, to 4,400/cm at 0.6 μm wavelength to 3.5/cm at 1.1 μm wavelength. Assuming zero reflection from both front and rear surfaces at each wavelength, calculate and sketch the generation rate of electron-hole pairs across a silicon cell of 300 μm thickness normalized to the surface generation rate.

2.2. In terms of the electronic properties of semiconductors, explain why the absorption coefficient increases with increasing photon energy, for energies near the semiconductor band gap (see Green, 1992 or similar for more information).

REFERENCES

Becquerel, E. (1839). "On electron effects under the influence of solar radiation". *Comptes Rendues*, 9, p 561.

Card, H.C. and Yang, E.S. (1977). "Electronic processes at grain boundaries in polycrystalline semiconductors under optical illumination". *IEEE Transactions on Electron Devices* ED-24, pp. 397-402.

Green, M.A. (1992), *Solar Cells - Operating Principles, Technology and System Application*, University of NSW, Kensington, Australia.

Neville, R.C. (1978). *Solar Energy Conversion: The Solar Cell*, Elsevier, Amsterdam.

Chapter 3

THE BEHAVIOUR OF SOLAR CELLS

3.1 EFFECT OF LIGHT

A silicon solar cell is a diode formed by joining p-type(typically boron doped) and n-type (typically phosphorous doped) silicon. Light shining on such a cell can behave in a number of ways, as illustrated in Figure 3.1. To maximise the power rating of a solar cell, it must be designed so as to maximise desired absorption (3) and absorption after reflection (5).

The electric field Ê at the p-n junction sweeps electrons to the n side and holes to the p side. The ideal flow at short circuit is shown in Figure 3.2. However, some electron-hole pairs get lost before collection, as shown in Figure 3.3.

In general, the closer the point of e - h generation to the p-n junction, the better the chance of "collection". "Collected carriers" are those which generate a finite current when V = 0. Chances of collection are particularly good if the e- h pairs are generated within a "diffusion length" of the junction as discussed in Chapter 2.

The characteristic curves generated by plotting I against V for a diode, the "IV" curve, were shown in Figure 2.11 for I_o, with no light falling on the cell. Illumination of a cell merely adds to the normal "dark" currents in the diode so that the diode law becomes:

$$I = I_o [\exp(qV/nkT) - 1] - I_L$$ (3.1)
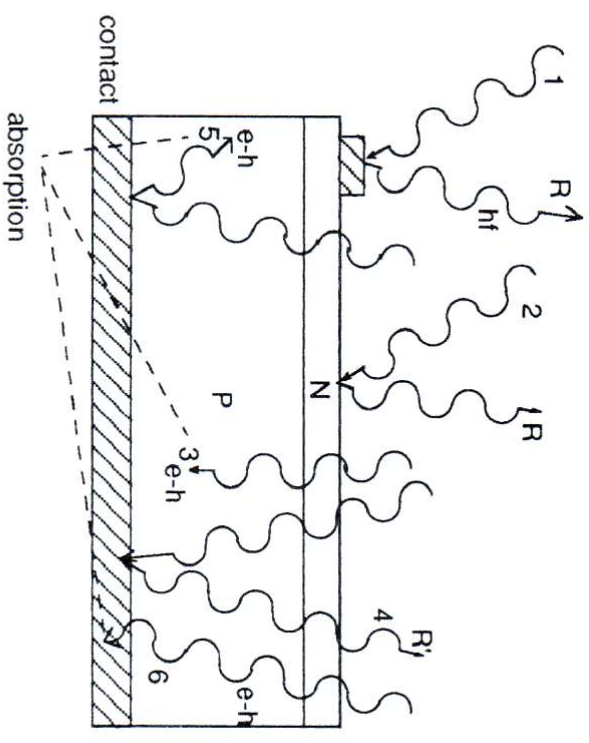
where I_L = light generated current.

Figure 3.1: Behaviour of light shining on a solar cell.

1. Reflection and absorption at top contact
2. Reflection at cell surface
3. Desired absorption
4. Reflection from rear out of cell - weakly absorbed light only
5. Absorption after reflection
6. Absorption in rear contact

contact

absorption

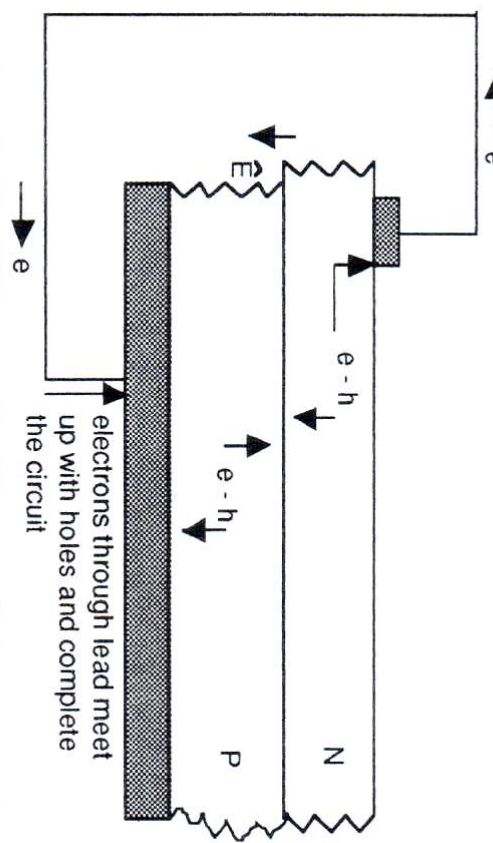electrons through lead meet up with holes and complete the circuit

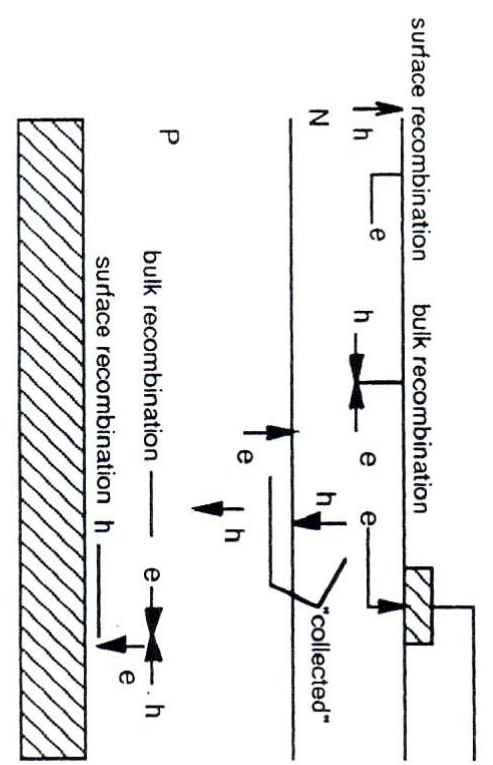Figure 3.2: The ideal short circuit flow of electrons and holes at a p-n junction.

Figure 3.3: Possible modes of recombination of electron-hole pairs, showing "collection" of carriers which do not recombine.
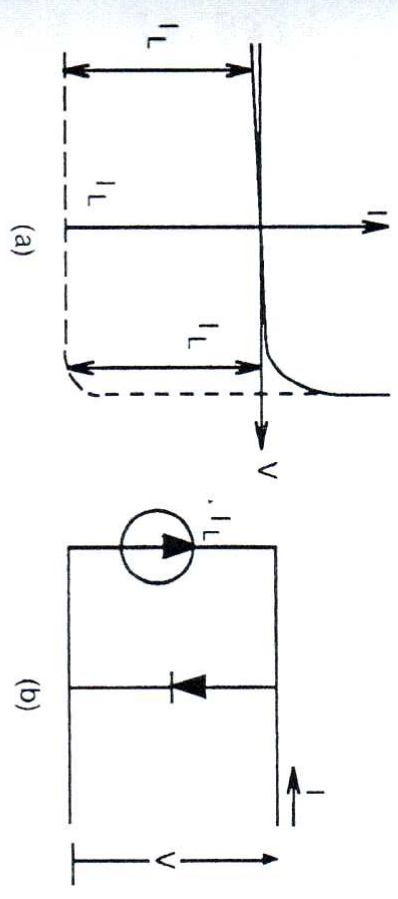
surface recombination   bulk recombination

bulk recombination

surface recombination

surface recombination

"collected"

Figure 3.4: The effect of light on the current-voltage characteristics of a p-junction.

(a)

(b)

The IV curve characterises the cell, with its power output being equal to the area of the rectangle in the bottom right hand quadrant of Figure 3.4(a). This IV curve is most often shown reversed, as in Figure 3.5, with the output curve in the first quadrant, and represented by:

The light has the effect of shifting the IV curve down into the fourth quadrant where power can be extracted from the diode, as shown in Figure 3.4.

$$I = I_L - I_o [\exp(qV/nkT) - 1] \qquad (3.2)$$
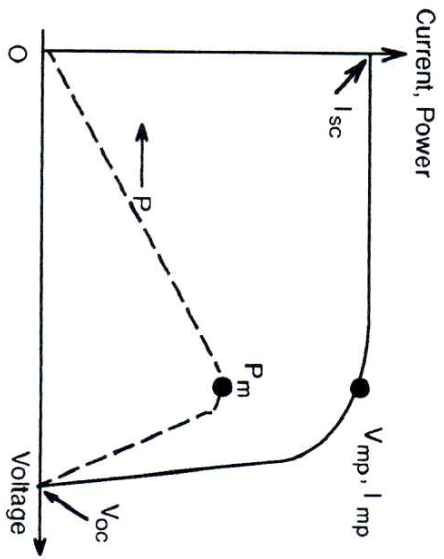
Figure 3.5: Typical representation of an IV curve, showing short circuit current (I_sc) and open circuit voltage (V_oc) points, as well as the maximum power point (V_mp, I_mp).

The two limiting parameters used to characterise the output of solar cells for given irradiance, operating temperature and area are (Shockley and Queisser, 1961):

Short-circuit current, I_sc, the maximum current, at zero voltage. Ideally, if $V = 0$, $I_{sc} = I_L$. Note that I_{sc} is directly proportional to the available sunlight.

Open-circuit voltage, V_oc, the maximum voltage, at zero current. V_{oc} increases logarithmically with increased sunlight. This characteristic makes solar cells ideally suited to battery charging.

Note that at $I = 0$:

$$V_{oc} = \frac{nkT}{q}\ln\left(\frac{I_L}{I_o} + 1\right) \qquad (3.3)$$

For each point on the IV curve, the product of the current and voltage represents the power output for that operating condition. A solar cell can also be characterised by its **maximum power point**, when the product $V_{mp} * I_{mp}$ is at its maximum value. The maximum power output of a cell is graphically given by the largest rectangle that can be fitted under the IV curve, ie.:

$$d(IV)/dV = 0$$

giving

$$V_{mp} = V_{oc} - \left(\frac{nkT}{q}\right)\ln\left\{\frac{V_{mp}}{nkT/q} + 1\right\} \qquad (3.4)$$

i.e., if n = 1.3 and V_{oc} = 600 mV, as for a typical silicon cell, V_{mp} is about 93 mV smaller than V_{oc}.

The power output at the maximum power point under strong sunlight (1 kW/m²) is known as the "peak power" of the cell. Hence photovoltaic panels are usually rated in terms of their "peak" watts, W_p.

The **Fill Factor, FF**, is a measure of the junction quality and series resistance of a cell. It is defined as the maximum power/$I_{sc}V_{oc}$ i.e.,

$$Fill\ Factor\ (FF) = \frac{V_{mp}\ I_{mp}}{V_{oc}\ I_{sc}} \qquad (3.5)$$

$$P_m = (V_{oc} \times I_{sc} \times FF) \qquad (3.6)$$

Obviously, the nearer the fill factor is to unity, the higher the quality of the cell. Ideally, it is a function only of the open-circuit voltage and can be calculated using the approximate empirical expression (Florida Solar Energy Centre, 1987)

$$FF = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1} \qquad (3.7)$$

where v_{oc} is defined as a "normalized V_{oc}":

$$v_{oc} = \frac{V_{oc}}{nkT/q} \qquad (3.8)$$

The above expression applies to ideal cases only, with no parasitic resistance losses, and is accurate to about 1 digit in the fourth decimal place for these cases.

3.2 SPECTRAL RESPONSE

Solar cells respond to individual photons in incident light by absorbing them to produce an electron-hole pair, provided the photon energy, E_{ph}, is greater than the bandgap energy, E_G. Photon energy in excess of E_G is quickly dissipated as heat, as shown in Figure 3.6.
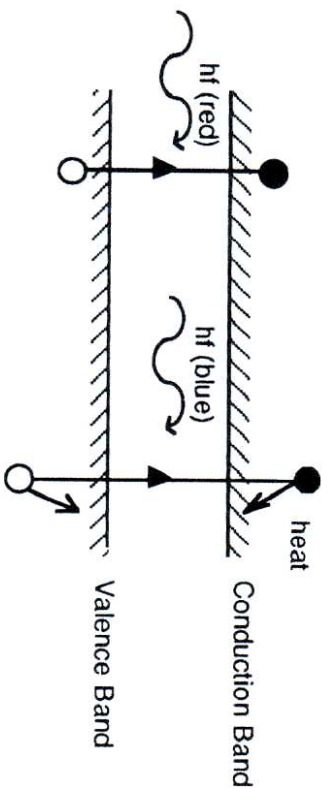
Figure 3.6: The creation of electron-hole pairs and dissipation of energy in excess of E_G.

The quantum efficiency (Q.E.) of a solar cell is defined as the number of electrons moving from the valence to the conduction band per incident photon. The quantum efficiency is limited by its bandgap. The longest wavelength for which this is finite is limited by its bandgap. Maximum use can only be made of incoming sunlight if bandgaps are in the range 1.0-1.6 eV. This effect alone acts to limit the maximum achievable efficiency of solar cells to 44% (Shockley and Queisser, 1961). Silicon's bandgap, at 1.1 eV, is close to optimum, while that of gallium arsenide, at 1.4 eV, is even better, in principle. Figure 3.7 illustrates the dependence of ideal quantum efficiency on bandgap.

$\lambda_G = hc/E_G$
$= 1.24/E_G$
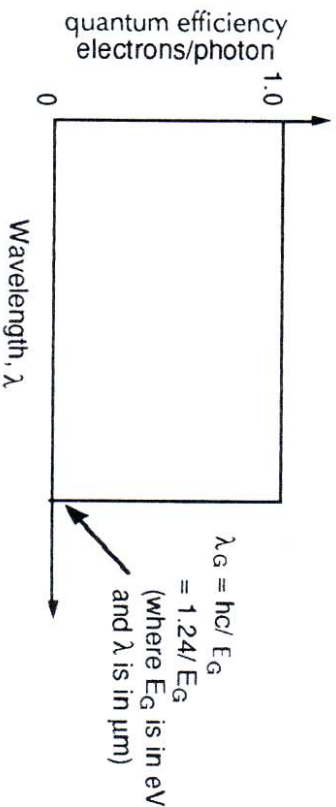(where E_G is in eV and λ is in μm)

Figure 3.7: Bandgap limitations on the quantum efficiency of Si solar cells.

Also of interest is the spectral responsivity of a solar cell, given by the Amps generated per Watt of incident light. Ideally this increases with wavelength. However, at short wavelengths, cells cannot utilise all the energy in the photons, while, at long wavelengths, the weak absorption of light means that most is generated a long way from the collecting junction and the finite diffusion length in the cell material limits the cell's response.
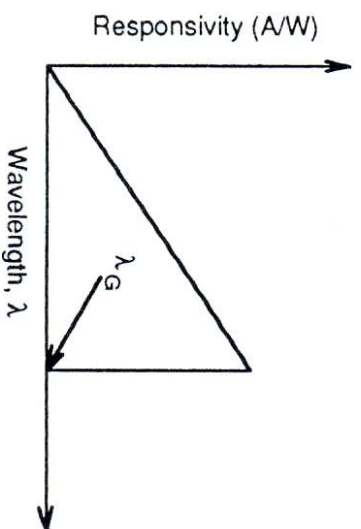

Figure 3.8: The quantum limit of spectral responsivity as a function of wavelength.

Spectral responsivity can be calculated as follows:

$$A/W = \frac{q \times \text{electron flux}}{\frac{hc}{\lambda} \times \text{photon flux}}$$
$$= \frac{q\lambda}{hc} \times Q.E.$$

(3.9)

where $A/W \to 0$ as $\lambda \to 0$, since there are fewer photons in each Watt of incident light.

This strong wavelength dependence of responsivity makes cell performance in turn strongly dependent on the spectral content of sunlight. In addition, optical and recombination losses mean that actual cells can only approach these ideals.

3.3   EFFECT OF TEMPERATURE

The operating temperature of solar cells is determined by the ambient air temperature, by the characteristics of the module in which it is encapsulated (see Section 5.8), by the intensity of sunlight falling on the module, and by other variables such as wind velocity.

I_0 increases with temperature according to the equation:

$$I_o = BT^\gamma \exp\left(\frac{-E_{GO}}{kT}\right)$$

(3.10)

Where B is independent of temperature; E_{GO} is the linearly extrapolated zero temperature band gap of the semiconductor

making up the cell (Green, 1992) and γ includes the temperature dependencies of the remaining parameters determining I_0.

The short-circuit current, I_{sc}, increases with temperature, since the band gap energy, E_G, decreases and more photons have enough energy to create e - h pairs. However, this is a small effect:

$$\frac{1}{I_{sc}} \frac{dI_{sc}}{dT} \approx +0.0006/°C \; for \; Si \qquad (3.11)$$

The main effect of increasing temperature for silicon solar cells is a reduction in V_{oc}, the fill factor and hence the cell output.

The temperature dependency of V_{oc} and FF for silicon is approximated by the following equations:

$$\frac{dV_{oc}}{dT} = -\left[\frac{V_{GO} - V_{oc} + \gamma(kT/q)}{T}\right] \approx -2mV/°C \qquad (3.12)$$

$$\frac{1}{V_{oc}} \frac{dV_{oc}}{dT} \approx -0.003/°C \; for \; Si \qquad (3.13)$$

$$\frac{1}{FF} \frac{d(FF)}{dT} \approx \left[\frac{1}{V_{oc}} \frac{dV_{oc}}{dT} - \frac{1}{T}\right]/6 \approx -0.0015/°C \; for \; Si \qquad (3.14)$$

The effect of temperature on the maximum power output, P_m, is:

$$\frac{1}{P_m} \frac{dP_m}{dT} \approx -(0.004 \, to \, 0.005)/°C \; for \; Si \qquad (3.15)$$

It should be noted that the higher the V_{oc}, the smaller the expected T dependence. These effects are illustrated in Figure 3.9.

3.4 EFFECT OF PARASITIC RESISTANCES

Solar cells generally have a parasitic series and shunt resistance associated with them, as shown in Figure 3.10. Both types of parasitic resistance act to reduce the fill-factor.

The major contributors to the series resistance, R_s, are the bulk resistance of the semiconductor material, the metallic contacts and interconnections and the contact resistance between the metallic contacts and the semiconductor. The effect of series resistance is shown in Figure 3.11.
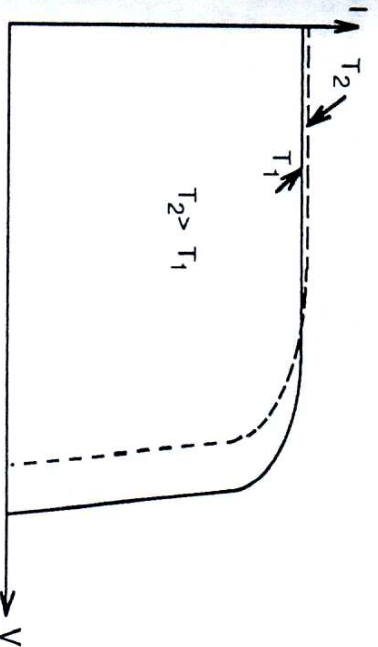
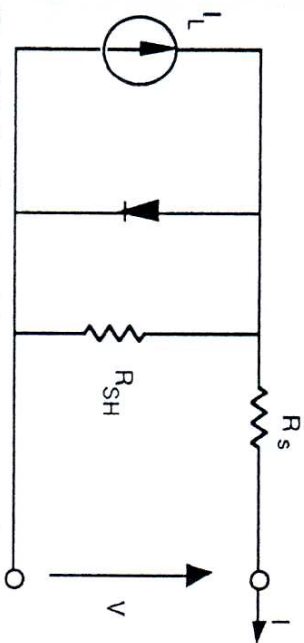Figure 3.9: The effect of temperature on the IV characteristics of a solar cell.

Figure 3.10: Parasitic series and shunt resistances in a solar cell circuit.
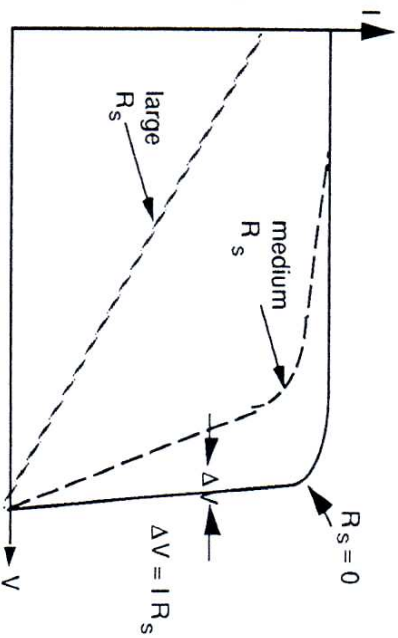
Figure 3.11: The effect of series resistance on fill factor.

The shunt resistance, R_{SH}, is due to p-n junction non-idealities and impurities near the junction, which cause partial shorting of the junction, particularly near cell edges.

Since the fill factor determines the power output of the cell, the maximum power output is related to the series resistance, as given approximately by:

$$P_m \approx \left(V_{mp} - I_{mp} R_s\right) I_{mp}$$
$$\approx P_{mp}\left(1 - \frac{I_{mp}}{V_{mp}} R_s\right)$$
$$\approx P_o\left(1 - \frac{I_{sc}}{V_{oc}} R_s\right)$$

(3.16)

If the characteristic resistance of a solar cell is defined as (Green, 1982):

$$R_{CH} = V_{oc}/I_{sc}$$

(3.17)

it is possible to define a "normalized Rs" such that:

$$r_s = R_s/R_{CH}$$

(3.18)

Hence

$$FF = FF_o(1 - r_s)$$

(3.19)

or, empirically but more accurately:

$$FF_s = FF_o(1 - 1.1 r_s) + r_s^2/5.4$$

(3.20)

which is valid for $r_s < 0.4$ and $v_{oc} > 10$. Similarly, for shunt resistance, it is possible to define:

$$r_{sh} = R_{SH}/R_{CH}$$

(3.21)

Then, as before:

$$FF \approx FF_o(1 - 1/r_{sh})$$

(3.22)

or, again more accurately (Green, 1992):

$$FF_{sh} = FF_o\left\{1 - \frac{(v_{oc} + 0.7)}{v_{oc}} \frac{FF_o}{r_{sh}}\right\}$$

(3.23)

which is valid for $r_{sh} > 0.4$. The effect of shunt resistance on fill factor is shown in Figure 3.12.
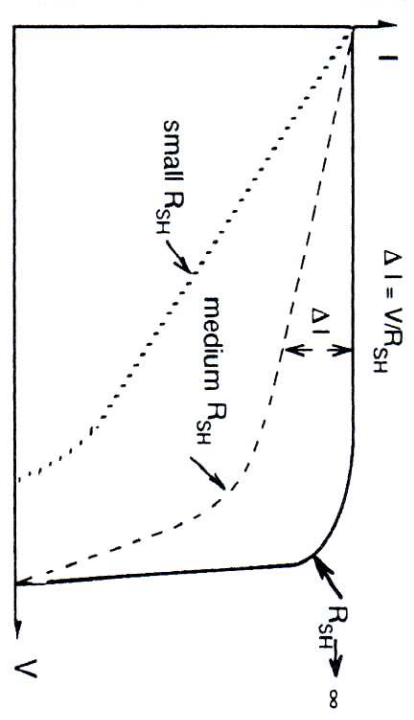

Figure 3.12: The effect of shunt resistance on fill factor in a solar cell.

In the presence of both series and shunt resistances, the IV curve of the solar cell is given by:

$$I = I_L - I_0\left\{\exp\left[\frac{V + IR_s}{nkT/q}\right] - 1\right\} - \frac{(V + IR_s)}{R_{SH}}$$

(3.24)

To combine the effect of both series and shunt resistances, the expression for FF_{sh} derived above, can be used, with FF_o replaced by FF_s (Green, 1992).

EXERCISES

3.1 (a) Taking the silicon bandgap as 1.12 eV, and assuming unity quantum efficiency as in Figures 3.7 and 3.8, calculate the upper limit on the short-circuit current density of a silicon solar cell at 300K for the standard "unnormalized" global AM1.5 spectrum supplied in tabulated form in Appendix B.

(b) Given that, near operating temperatures, the silicon bandgap decreases by 0.273 mV/°C, calculate the normalized temperature coefficient of this current limit at 300K:

$$\left(\frac{1}{I_{sc}} \frac{dI_{sc}}{dT} \right)$$

3.2 (a) A silicon solar cell (bandgap 1.12 eV) is uniformly illuminated by monochromatic light of wavelength 800 nm and intensity 20 mW/cm². Given that its quantum efficiency at this wavelength is 0.80, calculate the short-circuit current of the cell if its area is 4 cm².

(b) For the same quantum efficiency, what would be the value of this current if the cell were made from a semiconductor of bandgap: (i) 0.7 eV; (ii) 2.0 eV.

(c) For the silicon cell of part (a), calculate the open-circuit voltage, fill factor and energy conversion efficiency, given that its ideality factor is 1.2 and dark saturation current density is 1 pA/cm².

(d) Estimate the range of values of (i) series resistance; (ii) shunt resistance which would cause a relative reduction in the fill factor and energy conversion efficiency of less than 5%.

3.3 (a) When the cell temperature is 300K, a certain silicon cell of 100 cm² area gives an open circuit voltage of 600 mV and a short circuit current output of 3.3A under 1 kW/m² illumination. Assuming that the cell behaves ideally, what is its energy conversion efficiency at the maximum power point?

(b) What would be its corresponding efficiency if the cell had a series resistance of 0.1 Ω and a shunt resistance of 3 Ω?

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