

## Chapter 2

# Photons In, Electrons Out: Basic Principles of PV

### 2.1. Introduction

In Chapter 1 the solar cell was introduced and its performance characteristics, in response to applied bias and light, were defined. In this chapter we address some of the thermodynamic aspects of photovoltaic solar energy conversion. The chapter is organised as follows: first the radiant power available from the sun is defined; the photovoltaic cell is distinguished from other types of solar energy converter and the question of how much electrical work can be extracted is addressed; the principle of detailed balance is introduced and used to calculate the performance characteristics of an ideal photovoltaic energy converter. We shall see that efficiency depends on the band gap of the absorbing material and the incident spectrum. Finally, the properties which are desirable for high efficiency in real photovoltaic materials and devices are discussed.

### 2.2. The Solar Resource

The sun emits light with a range of wavelengths, spanning the ultraviolet, visible and infrared sections of the electromagnetic spectrum. Figure 2.1 shows the amount of radiant energy received from the sun per unit area per unit time — the solar irradiance — as a function of wavelength at a point outside the Earth's atmosphere. Solar irradiance is greatest at visible wavelengths, 300–800 nm, peaking in the blue–green.

This extraterrestrial spectrum resembles the spectrum of a *black body* at 5760 K. A black body emits quanta of radiation — photons — with a distribution of energies determined by its characteristic temperature,  $T_s$ . At a point  $\mathbf{s}$  on the surface of the black body the number of photons with energy in the range  $E$  to  $E + dE$  emitted through unit area per unit solid

angle per unit time, the *spectral photon flux*  $\beta_s(E, \mathbf{s}, \theta, \phi)$ , is given by

$$\beta_s(E, \mathbf{s}, \theta, \phi) d\Omega \cdot d\mathbf{S} dE = \frac{2}{h^3 c^2} \left( \frac{E^2}{e^{E/k_B T_s} - 1} \right) d\Omega \cdot d\mathbf{S} dE \quad (2.1)$$

where  $d\mathbf{S}$  the element of surface area around  $\mathbf{s}$  and  $d\Omega$  the unit of solid angle around the direction of emission of the light  $(\theta, \phi)$ . The flux issued normal to the surface is given by the component of  $\beta_s$  integrated over solid angle and resolved along  $d\mathbf{S}$ ,

$$\begin{aligned} b_s(E, \mathbf{s}) dS dE &= \int_{\Omega} \beta_s(E, \mathbf{s}, \theta, \phi) \cdot \cos \theta d\Omega \cdot d\mathbf{S} dE \\ &= \frac{2F_s}{h^3 c^2} \left( \frac{E^2}{e^{E/k_B T_s} - 1} \right) dS dE \end{aligned} \quad (2.2)$$

where  $F_s$  is a geometrical factor which arises from integrating over the relevant angular range. Just at the surface of the black body this range is a hemisphere and  $F_s = \pi$ . Away from the surface, the angular range is reduced and

$$F_s = \pi \sin^2 \theta_{\text{sun}} \quad (2.3)$$

where  $\theta_{\text{sun}}$  is the half angle subtended by the radiating body to the point where the flux is measured. For the sun as seen from the earth,  $\theta_s = 0.26^\circ$  so that  $F_s$  is reduced by a factor of  $4.6 \times 10^4$  to  $2.16 \times 10^{-5} \pi$ . If the temperature at all points  $\mathbf{s}$  on the surface of the black body is the same, then the argument  $\mathbf{s}$  can be dropped from  $b_s$ , and Eq. 2.2 can be written

$$b_s(E) = \frac{2F_s}{h^3 c^2} \left( \frac{E^2}{e^{E/k_B T_s} - 1} \right). \quad (2.2)$$

In the remaining sections of this chapter we will use  $b_s$  and  $F_s$  to represent the spectral photon flux and geometrical factor for the sun.



Box 2.1. The angular resolved photon flux density,  $\beta$ , is the number of photons of given energy passing through unit area in unit time, per unit solid angle. It is defined on an element of surface area, and its direction is defined by the angle to the surface normal,  $\theta$ , and an azimuthal angle,  $\phi$ , projected on the plane of the surface element. In structures with planar symmetry it is sufficient to know the photon flux density resolved along the normal to the surface,  $b$ .  $b$  is obtained by integrating the components of  $\beta$  normal to the surface over solid angle.

The emitted energy flux density or *irradiance*,  $L(E)$ , is related to the photon flux density through

$$L(E) = Eb_s(E). \quad (2.4)$$

Integrating Eq. 2.4 over  $E$  gives the total emitted power density,  $\sigma_s T_s$ , where  $\sigma_s$  is Stefan's constant,

$$\sigma_s = \frac{2\pi^5 k^4}{15c^2 h^3}.$$

At the sun's surface this is a power density of  $62 \text{ MW m}^{-2}$ . At a point just outside the Earth's atmosphere the solar flux is reduced (on account of the reduced angular range of the sun) and the solar power density is reduced to  $1353 \text{ W m}^{-2}$ . In Fig. 2.1 the extraterrestrial solar spectrum is compared with the spectrum of a  $5760 \text{ K}$  black body, reduced by the factor  $4.6 \times 10^4$ . The higher  $T_s$ , the higher the average energy of the emitted radiation. A black body at the temperature of the Earth,  $T_s = 300 \text{ K}$ , emits most strongly in the far infrared and its radiation cannot be seen. For the sun, with  $T_s = 5760 \text{ K}$  the emission is strongest at visible wavelengths. A hotter sun would emit light that appears blue to us, with a spectrum shifted to shorter wavelengths on Fig. 2.1, and a cooler sun would appear red.

On passing through the atmosphere, light is absorbed and scattered by various atmospheric constituents, so that the spectrum reaching the Earth's

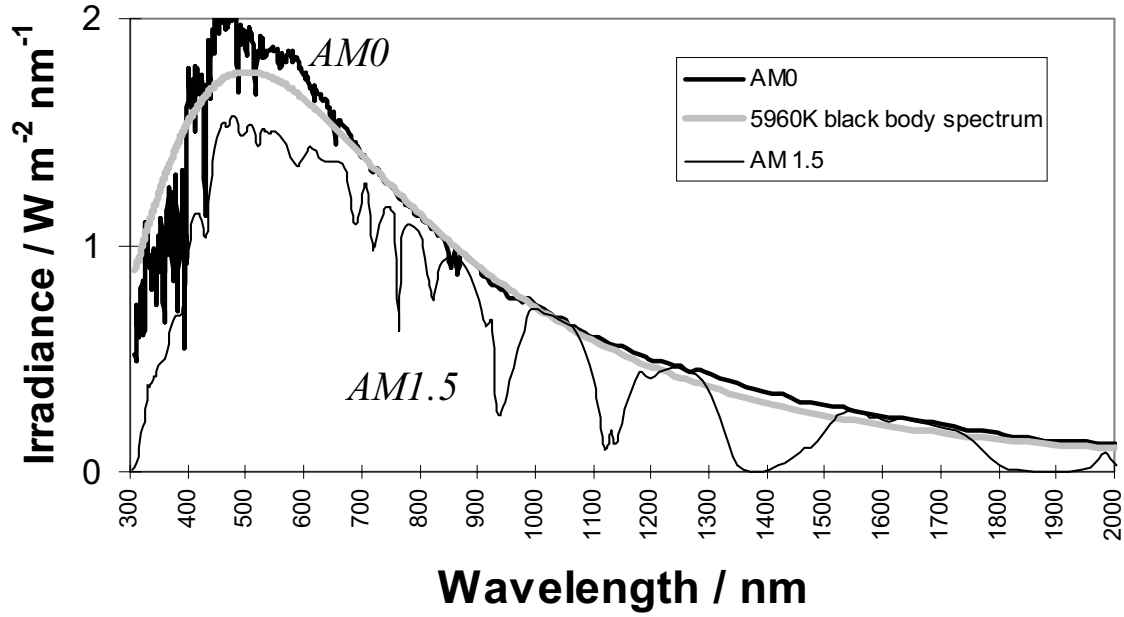


Fig. 2.1. Extra-terrestrial (Air Mass 0) solar spectrum (black line) compared with the 5760 K black body spectrum reduced by the factor  $4.6 \times 10^4$  (thick grey line) and with the standard terrestrial (Air Mass 1.5) spectrum (thin grey line).

surface is both attenuated and changed in shape. Light of wavelengths less than 300 nm is filtered out by atomic and molecular oxygen, ozone, and nitrogen. Water and  $\text{CO}_2$  absorb mainly in the infrared and are responsible for the dips in the absorption spectrum at 900, 1100, 1400 and 1900 nm ( $\text{H}_2\text{O}$ ) and at 1800 and 2600 nm ( $\text{CO}_2$ ). Attenuation by the atmosphere is quantified by the ‘Air Mass’ factor,  $n_{\text{AirMass}}$  defined as follows

$$n_{\text{AirMass}} = \frac{\text{optical path length to Sun}}{\text{optical path length if Sun directly overhead}} = \text{cosec } \gamma_s. \quad (2.5)$$

where  $\gamma_s$  is the angle of elevation of the sun, as shown in Fig. 2.2. The Air Mass  $n_{\text{AirMass}}$  spectrum is an extraterrestrial solar spectrum attenuated by  $n_{\text{AirMass}}$  thicknesses of an Earth atmosphere of standard thickness and composition.

The standard spectrum for temperature latitudes is *Air Mass 1.5*, or AM1.5, corresponding to the sun being at an angle of elevation of  $42^\circ$ . This atmospheric thickness should attenuate the solar spectrum to a mean irradiance of around  $900 \text{ W m}^{-2}$ . However, for convenience, the standard terrestrial solar spectrum is defined as the AM1.5 spectrum normalised so that the integrated irradiance is  $1000 \text{ W m}^{-2}$ . Actual irradiances clearly vary on account of seasonal and daily variations in the position of the sun

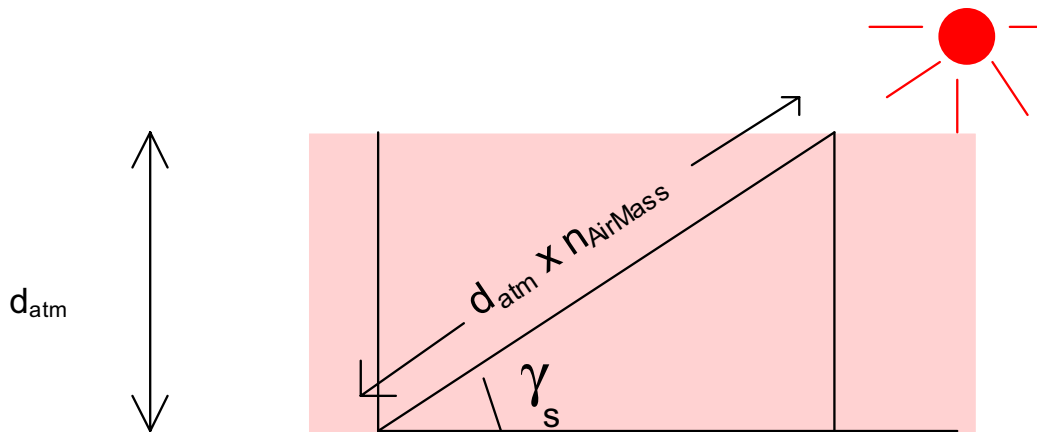


Fig. 2.2. If the atmosphere has thickness  $d_{atm}$ , then when the sun is at an angle of elevation  $\gamma_s$ , light from the sun has to travel through a distance  $d_{atm} \times \text{cosec } \gamma_s$  through the atmosphere to an observer on the Earth's surface. The optical depth of the atmosphere is increased by a factor  $n_{AirMass} = \text{cosec } \gamma_s$  compared to when the sun is directly overhead.

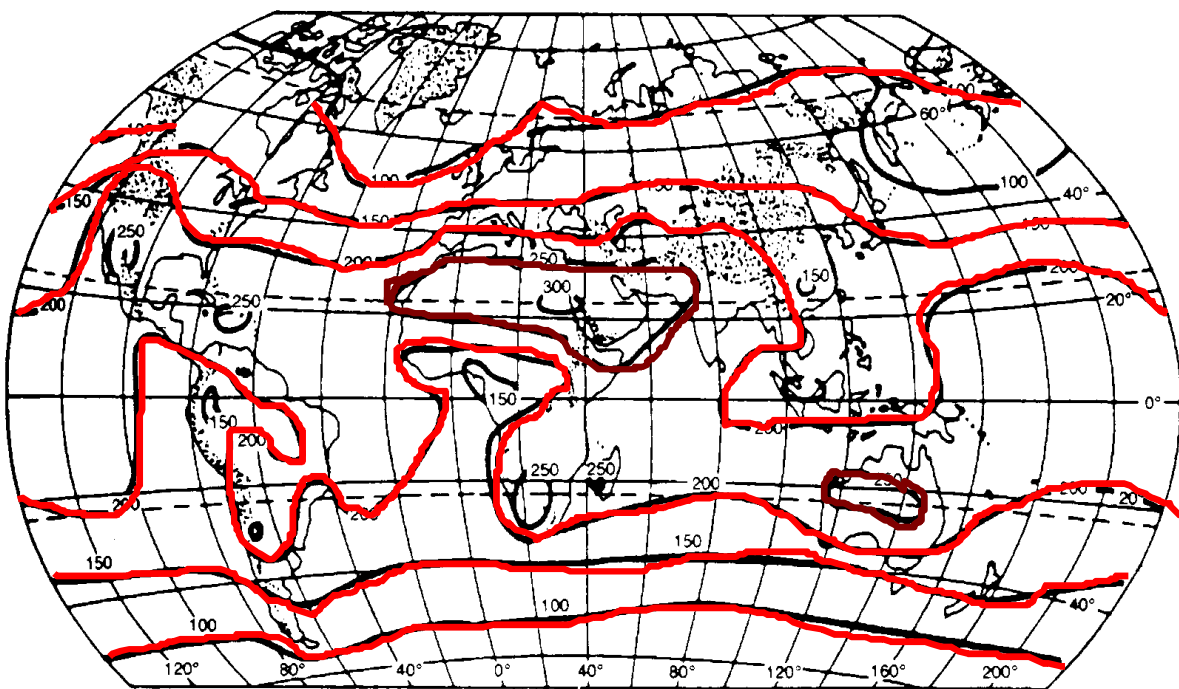


Fig. 2.3. Global distribution of annual average solar irradiance. The values on the irradiance contours are given in  $\text{W m}^{-2}$ .

and orientation of the Earth and condition of the sky. Averaged global irradiances vary from less than  $100 \text{ W m}^{-2}$  at high latitudes to over  $300 \text{ W m}^{-2}$  in the sunniest places (usually, desert area in continental interiors), as shown in Fig. 2.3. (Solar radiation and spectral variations are discussed by [Gottschalg, 2001].)

For efficient solar collection, the solar collector should be directly facing the sun. However, variations in the position of the sun mean that any flat plate collector in a fixed position will face the sun only part of the time. Tracking systems can be used to follow the sun but these increase the cost.

Scattering of light by the atmosphere means a fraction of the light is *diffuse*, *i.e.*, incident from all angles rather than direct from the sun. This fraction is around 15% on average, but larger at higher latitudes, and in regions where there is a significant amount of cloud cover. Diffuse light presents different challenges for photovoltaic conversion. Since the light rays are not parallel, they cannot be refracted or concentrated. Materials with rough surfaces are relatively better suited for diffuse light than perfectly flat surfaces and are less sensitive to movements of the sun.

### 2.3. Types of Solar Energy Converter

The photovoltaic device should be distinguished from both solar thermal and photochemical energy converters. Solar thermal energy conversion results from the heat exchange between a hot body (the sun) and a cool one (the solar thermal device). Photochemical conversion is, like photovoltaic conversion, a quantum energy conversion process but one which results in a permanent increase in chemical potential rather than electric power. To distinguish these different types of solar energy converter, we need to consider the different modes of energy transfer from the sun.

The radiant energy absorbed by a device can either increase the kinetic energy of the atoms and electrons in the absorbing material (the internal energy), or it can increase the potential energy of the electrons. Which of these happens depends upon the material and how it is connected to the outside world. In a solar thermal converter the radiant energy absorbed is converted mainly into internal energy and raises the temperature of the cell. The difference in temperature relative to the ambient means that the solar converter can operate as a heat engine and do work, for instance by driving a steam turbine to generate electric power. Solar thermal converters utilise the full range of solar wavelengths, including the infrared, and are designed to heat up easily. They are thermally insulated from the ambient to make the working temperature difference as large as possible.

A photovoltaic converter, on the other hand, is designed to convert the incident solar energy mainly into electrochemical potential energy. Absorption of a photon in matter causes the promotion of an electron to a state of higher energy (an *excited state*). For the extra electronic energy to

be extracted, the excited state should be separated from the ground state by an energy gap which is large compared to  $k_B T$ , where  $k_B$  is Boltzmann's constant. Therefore the material should contain two or more energy levels, or bands, which are separated by more than  $k_B T$ . In Chapter 3 we will see that a semiconductor is a very good example of such a system. The separation of the energy bands, or *band gap*, serves to maintain the excited electrons at the higher energy for a long time compared to the thermal relaxation time, so that they may be collected. Electrons in each of the different bands relax to form a local thermal equilibrium, called a *quasi thermal equilibrium*, with a different chemical potential, or, *quasi Fermi level*. In a two band system, the increase in electrochemical potential energy is given by the Gibbs free energy,  $N\Delta\mu$ , where  $N$  is the number of electrons promoted and  $\Delta\mu$  the difference in the chemical potentials between the excited population and the ground state population. The difference in  $\Delta\mu$  which results from the absorption of light is sometimes called the chemical potential of radiation. In equilibrium,  $\Delta\mu = 0$ . Extraction of electrochemical potential energy from light in this way is most effective when the ground state is full initially and the excited state is empty.

Unlike the solar thermal converter, the photovoltaic converter extracts solar energy only from those photons with energy sufficient to bridge the band gap. Since these mainly increase the electrochemical potential energy the increase in internal energy is much less. In practice, increased temperature can decrease the efficiency of photovoltaic conversion and so photovoltaic cells are usually designed to be in good thermal contact with the ambient.

To complete the photovoltaic conversion process, the excited electrons must be extracted and collected. This requires a mechanism for *charge separation*. Some intrinsic asymmetry is needed to drive the excited electrons away from their point of creation. (In general, charge separation involves positive holes and/or ions as well as electrons. We describe the process in terms of electrons for simplicity.) This can be provided by selective contacts such that carriers with raised  $\mu$  (excited state) are collected at one contact and those with low  $\mu$  (ground state) at the other. The difference in chemical potential between the contacts,  $\Delta\mu$ , then provides a potential difference between the terminals of the cell. Once separated, the charges should be allowed to travel without loss to an external circuit and do electrical work.

Photovoltaic conversion is similar to photochemical energy conversion (*e.g.* in photosynthesis), in that radiant energy produces an increase in electronic potential energy, rather than heat. In the case of photosynthesis

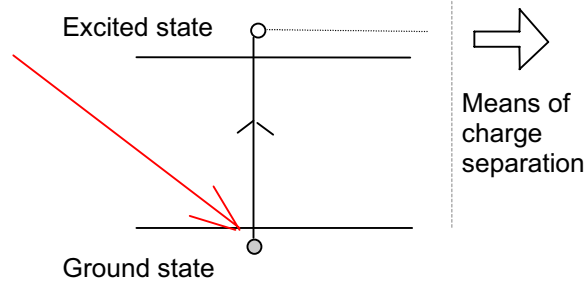


Fig. 2.4. Excitation and charge separation. After an electron is promoted to a higher energy level by absorption of a photon of sufficient energy, it must be pulled away from the point of promotion by some mechanism for charge separation. The driving force for charge separation prevents the relaxation of the system to its initial state.

the excited electron population drives a chemical reaction, the conversion of  $\text{CO}_2$  and water into carbohydrate, rather than driving an electric current. But in either case the solar energy results in a net flux of electronic potential energy constituting work. The different modes of solar energy conversion are explained in detail by de Vos [de Vos, 1992].

In the following sections we will calculate the amount of work available from a photovoltaic device.

## 2.4. Detailed Balance

One of the fundamental physical limitations on the performance of a photovoltaic cell arises from the principle of detailed balance. As well as absorbing solar radiation the solar energy converter exchanges *thermal* radiation with its surroundings. Both the cell and the surrounding environment radiate long wavelength, thermal, photons on account of their finite temperature. The rate of emission of photons by the cell must be matched by the rate of photon absorption, so that in the steady state the concentration of electrons in the material remains constant.

### 2.4.1. In equilibrium

First we consider the cell in the dark, in thermal equilibrium with the ambient. Assuming that the ambient radiates like a black body at a temperature  $T_a$ , then, according to Eq. 2.1, it produces a spectral photon flux at a point  $s$  on the surface of the solar cell of

$$\beta_a(E, \mathbf{s}, \theta, \phi) d\Omega. d\mathbf{S} dE = \frac{2}{h^3 c^2} \left( \frac{E^2}{e^{E/k_B T_a} - 1} \right) d\Omega. d\mathbf{S} dE .$$

Integrating over directions, we obtain the incident flux of thermal photons normal to the surface of a flat plate solar cell

$$b_a(E) = \frac{2F_a}{h^3c^2} \left( \frac{E^2}{e^{E/k_B T_a} - 1} \right) \quad (2.6)$$

where the geometrical factor  $F_a = \pi$ , assuming that ambient radiation is received over a hemisphere. The equivalent *current density* absorbed from the ambient is

$$j_{\text{abs}}(E) = q(1 - R(E))a(E)b_a(E) \quad (2.7)$$

where  $a(E)$  is the probability of absorption of a photon of energy  $E$  and  $R(E)$  is the probability of photon reflection.  $j_{\text{abs}}(E)$  is the electron current density equivalent to the absorbed photon flux if each photon of energy  $E$  generates one electron.  $a(E)$  is known as the *absorbance* or *absorptivity*, and is determined by the absorption coefficient of the material and by the optical path length through the device.

To obtain the total equivalent current for photon absorption, Eq. 2.7 should be integrated over the surface of the solar collector. The result depends on the interface at the rear surface. If the rear surface contacts the air, then both sides contribute equally, and the equivalent current is  $2qA(1 - R(E))a(E)b_a(E)$  for a collector of area  $A$ . If the rear surface is in contact with a material of higher refractive index,  $n_s$ , the rate of photon absorption is enhanced by  $n_s^2$  over that surface, and the result is  $q(1 + n_s^2)A(1 - R(E))a(E)b_a(E)$ . In the case of a perfect reflector (which is capable of reflecting thermal photons) at the rear surface, the equivalent current for absorbed thermal photons is only  $qA(1 - R(E))a(E)b_a(E)$ . In this case the areas for thermal photon and solar photon absorption are the same, and the device efficiency is the greatest. In the following analysis we assume that this is the case.

As well as absorbing thermal photons, the cell *emits* thermal photons by spontaneous emission. Spontaneous emission is the conversion into a photon of the potential energy released when an excited electron relaxes to its ground state (Fig. 2.5). (Stimulated emission, discussed in Chapter 4, can be neglected since the solar cell operates in a limit where the excited state is almost empty.) This emission is necessary to maintain a steady state.

A cell in thermal equilibrium with its surroundings, *i.e.*, receiving no radiation other than from the ambient, has temperature  $T_a$  and emits thermal radiation characteristic of that temperature. If  $\varepsilon$  is the *emissivity* (or probability of emission of a photon of energy  $E$ ) the equivalent current

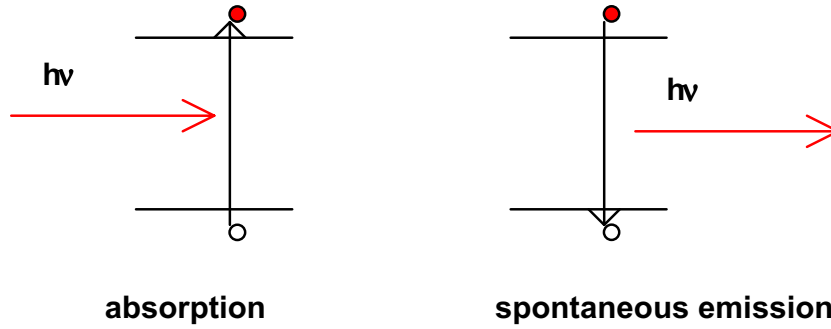


Fig. 2.5. Absorption and spontaneous emission. In spontaneous emission, also known as radiative recombination, the electron relaxes from excited state to ground state giving out its extra potential energy as a photon of light.

density for photon emission through the surface of the cell is given by

$$j_{\text{rad}}(E) = q(1 - R(E))\varepsilon(E)b_a(E). \quad (2.8)$$

In order to maintain a steady state, the current densities  $j_{\text{abs}}$  (Eq. 2.7) and  $j_{\text{rad}}$  (Eq. 2.8) must balance and therefore

$$\varepsilon(E) = a(E). \quad (2.9)$$

This is a result of *detailed balance*: In quantum mechanical terms, it results from the fact that the matrix element for optical transitions from ground to excited state and from excited to ground state must be identical.

#### 2.4.2. Under illumination

Under illumination by a solar photon flux  $b_s(E)$  (Eq. 2.2), the cell absorbs solar photons of energy  $E$  at a rate

$$(1 - R(E))a(E)b_s(E).$$

The equivalent current density for photon absorption includes a contribution from thermal photons, hence

$$j_{\text{abs}}(E) = q(1 - R(E))a(E) \left( b_s(E) + \left( 1 - \frac{F_s}{F_e} \right) b_a(E) \right) \quad (2.10)$$

where the coefficient of  $b_a$  is introduced to allow for the fraction of the incident ambient flux which has been replaced by solar radiation.

As a result of illumination, part of the electron population has raised electrochemical potential energy, and the system develops a chemical potential  $\Delta\mu > 0$ . In these conditions spontaneous emission is increased and

the rate of emission depends upon  $\Delta\mu$ . This makes sense since when more electrons are at raised energy, relaxation events are more frequent. According to a generalised form of Planck's radiation law, the spectral photon flux emitted from a body of temperature  $T_C$  and chemical potential  $\Delta\mu$  into a medium of refractive index  $n_s$  is given by

$$\beta(E, s, \theta, \phi) = \frac{2n_s^2}{h^3 c^2} \frac{E^2}{e^{(E-\Delta\mu)/k_B T_a} - 1} \quad (2.11)$$

per unit surface area and solid angle [Wuerfel, 1982; de Vos, 1992]. Integrating over the range of solid angle through which photons can escape ( $0 \leq \theta \leq \theta_c$ ) we obtain the photon flux emitted normal to the surface

$$b_e(E, \Delta\mu) = F_e \frac{2n_s^2}{h^3 c^2} \frac{E^2}{e^{(E-\Delta\mu)/k_B T_a} - 1} \quad (2.12)$$

where

$$F_e = \pi \sin^2 \theta_c = \pi \frac{n_0^2}{n_s^2} \quad (2.13)$$

and

$$\theta_c = \sin^{-1} \left( \frac{n_0}{n_s} \right)$$

by Snell's law, where  $n_0$  is the refractive index of the surrounding medium.

At a surface with air,  $n_0 = 1$ ,  $F_e \times n_s^2 = F_a = \pi$  and

$$b_e(E, \Delta\mu) = \frac{2F_a}{h^3 c^2} \frac{E^2}{e^{(E-\Delta\mu)/k_B T_a} - 1}. \quad (2.14)$$

Note that this result is the same whether the integration is taken over internal or external solid angle: internally,  $n_s$  must be retained but the angular range is limited to  $\theta_c$ , while externally  $n_s = 1$  but the angular range is a hemisphere.

Now if  $\varepsilon$  is the probability of photon emission, the equivalent current density for photon emission is

$$j_{\text{rad}}(E) = q(1 - R(E))\varepsilon(E)b_e(E, \Delta\mu). \quad (2.15)$$

It is easy to see that Eq. 2.15 reduces to Eq. 2.8 for the cell in equilibrium, where  $a = \varepsilon$  and  $\Delta\mu = 0$ . It is not immediately obvious how  $a(E)$  relates to  $\varepsilon(E)$  for the cell with  $\Delta\mu > 0$ . However, it has been shown elsewhere [Araujo, 1994] from a generalised detailed balance argument that Eq. 2.9

still holds, provided that  $\Delta\mu$  is constant through the device. That result will be used below without proof.

The *net* equivalent current density, from Eqs. 2.10 and 2.15 is,

$$\begin{aligned} j_{\text{abs}}(E) - j_{\text{rad}}(E) \\ = q(1 - R(E))a(E) \left( b_{\text{s}}(E) + \left( 1 + \frac{F_{\text{s}}}{F_{\text{a}}} \right) b_{\text{a}}(E) - b_{\text{e}}(E, \Delta\mu) \right). \end{aligned} \quad (2.16)$$

This may be divided into contributions from *net* absorption (in excess to that at equilibrium),

$$j_{\text{abs}(\text{net})}(E) = q(1 - R(E))a(E) \left( b_{\text{s}}(E) - \frac{F_{\text{s}}}{F_{\text{e}}} b_{\text{a}}(E) \right) \quad (2.17)$$

and the *net* emission, or *radiative recombination* current density

$$j_{\text{abs}(\text{net})}(E) = q(1 - R(E))a(E)(b_{\text{e}}(E, \Delta\mu) - b_{\text{e}}(E, 0)), \quad (2.18)$$

noting that  $b_{\text{a}}(E) = b_{\text{e}}(E, 0)$ . This radiative recombination is an unavoidable loss which means that absorbed solar radiant energy can never be fully utilised by the solar cell. Radiative recombination is discussed further in Chapter 4.

## 2.5. Work Available from a Photovoltaic Device

Now we have enough information to calculate the absolute limiting efficiency of a photovoltaic converter. We will consider a two band system for which the ground state (lower band) is initially full and the excited state (upper band) empty. The bands are separated by a band gap,  $E_{\text{g}}$ , so that light with  $E < E_{\text{g}}$  is not absorbed (see Fig. 2.6). We will assume that electrons in each band are in quasi thermal equilibrium at the ambient temperature  $T_{\text{a}}$  and the chemical potential for that band,  $\mu_{\text{i}}$ .

### 2.5.1. Photocurrent

Photocurrent is due to the net absorbed flux due to the sun, Eq. 2.17. Since the angular range of the sun is so small compared to the ambient, the second term in Eq. 2.17 is usually neglected. If each electron has a probability,  $\eta_{\text{c}}(E)$ , of being collected, we obtain the photocurrent density

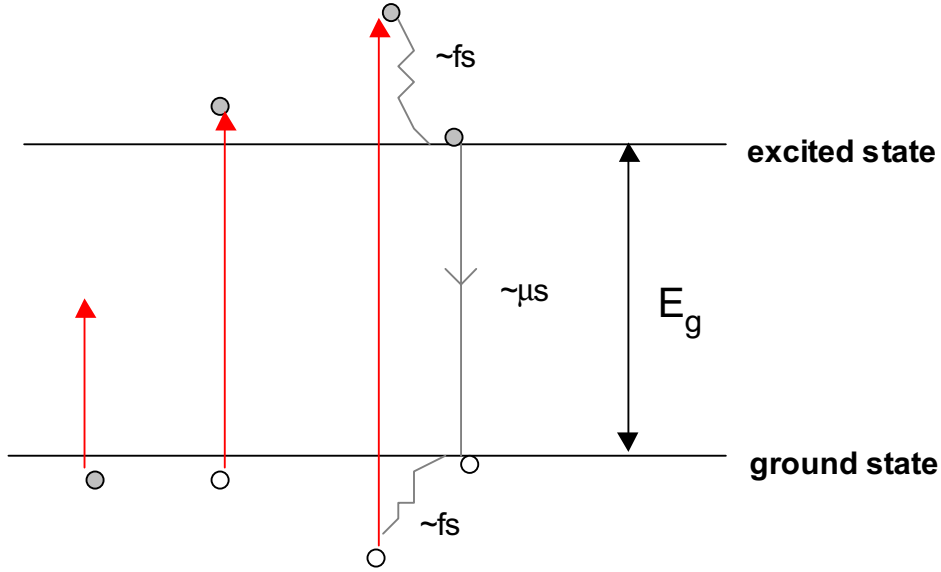


Fig. 2.6. Two band photoconverter. Photons with energy  $E < E_g$  cannot promote an electron to the excited state. Photons with  $E \geq E_g$  can raise the electron but any excess energy is quickly lost as heat as the carriers relax to the band edges. An absorbed photon with  $E \gg E_g$  achieves the same result as a photon with  $E = E_g$ . For this reason it is the incident photon flux and not the photon energy density which determines the photogeneration. Once excited the electrons remain in the excited state for a relatively long time.

at short circuit by integrating  $j_{\text{abs}}$  over photon energies

$$J_{\text{sc}} = q \int_0^{\infty} \eta_c(E)(1 - R(E))a(E)b_s(E)dE. \quad (2.19)$$

This is identical to Eq. 1.1 with the quantum efficiency  $QE(E)$  given by the product of the collection and absorption efficiencies.

$$J_{\text{sc}} = q \int_0^{\infty} QE(E)b_s(E)dE \quad (1.1)$$

For the case of the most efficient solar cell we will suppose that we have a perfectly absorbing, non-reflecting material so that that *all* incident photons of energy  $E > E_g$  are absorbed to promote exactly one electron to the upper band. We further suppose perfect charge separation so that all electrons which survive radiative recombination are collected by the negative terminal of the cell and delivered to the external circuit (*i.e.*  $\eta_c(E) = 1$ ). This gives the maximum photocurrent for that band gap, assuming that multiple carrier generation — the promotion of *more* than one electron by

an absorbed photon — does not happen. Then

$$QE(E) = a(E) = \begin{cases} 1 & E \geq E_g \\ 0 & E < E_g \end{cases} \quad (2.20)$$

and

$$J_{sc} = q \int_{E_g}^{\infty} b_s(E) dE. \quad (2.21)$$

Photocurrent is then a function *only* of the band gap and the incident spectrum. Clearly, the lower  $E_g$ , the greater will be  $J_{sc}$ . It is also clear from Eq. 2.21 that it is necessary to define the spectrum for any statement of efficiency.

### 2.5.2. Dark current

Dark current is the current that flows through the photovoltaic device when a bias is applied in the dark. We will suppose that in the ideal cell material no carriers are lost through non-radiative recombination, for example at defects within the material. The only loss process considered is the unavoidable radiative relaxation of electrons through spontaneous emission, described above. The dark current density due to this process is given by integrating  $j_{rad}$  over photon energy and, for a flat plate cell with perfect rear reflector, is given by

$$J_{rad}(\Delta\mu) = q \int (1 - R(E))a(E)(b_e(E, \Delta\mu) - b_e(E, 0))dE, \quad (2.22)$$

assuming that  $\Delta\mu$  is constant over the surface of the cell and using the detailed balance result,  $a(E) = \varepsilon(E)$ . In ideal material with lossless carrier transport  $\Delta\mu$  can be further assumed constant *everywhere* and equal to  $q$  times the applied bias  $V$  [Araujo, 1994]. Then, assuming that dark current and photocurrent can be added, as in Eq. 1.3

$$J(V) = J_{sc} - J_{dark}(V),$$

we obtain for the net cell current density,

$$J(V) = q \int_0^{\infty} (1 - R(E))a(E)\{b_s(E) - (b_e(E, qV) - b_e(E, 0))\}dE. \quad (2.23)$$

For the special case of the step-like absorption function (Eq. 2.20),

$$J(V) = q \int_{E_g}^{\infty} \{b_s(E) - (b_e(E, qV) - b_e(E, 0))\} dE, \quad (2.24)$$

$J(V)$  is strongly bias dependent through the exponential term in Eq. 2.12 and has the approximate form

$$J(V) = J_{sc} - J_0(e^{qV/k_B T} - 1)$$

where  $J_0$  is a (temperature dependent) constant for the particular material. This resembles the ideal diode Eq. 1.4.

The net electron current is thus due to the difference between the two photon flux densities: the absorbed flux, which is distributed over a wide range of photon energies above the threshold  $E_g$ , and the emitted flux, which is concentrated on photon energies near  $E_g$ . As  $V$  increases, the emitted flux increases and the net current decreases. At the open circuit voltage  $V_{oc}$  the total emitted flux exactly balances the total absorbed flux and the net current is zero. If  $V$  is increased still further, the emitted flux exceeds the absorbed and the cell begins to act like a light emitting device, giving out light in return for the applied electrical potential energy. Note that  $V_{oc}$  must always be less than  $\frac{E_g}{q}$ . The spectral fluxes leading to these regimes are illustrated in Fig. 2.7(a), while Fig. 2.7(b) illustrates the resulting  $J(V)$  curves.

### 2.5.3. Limiting efficiency

To calculate the power conversion efficiency we need to calculate the incident and extracted *power* from the photon fluxes. The incident power density is obtained simply by integrating the incident irradiance (Eq. 2.4) over photon energy,

$$P_s = \int_0^{\infty} E b_s(E_s) dE. \quad (2.25)$$

For the output power we need to know the electrical potential energy of the extracted photo-electrons. For the ideal photoconverter it is assumed that no potential is lost through resistances anywhere in the circuit. Therefore all collected electrons should have  $\Delta\mu$  of electrical potential energy and deliver  $\Delta\mu$  of work to the external circuit. Since  $\Delta\mu = qV$  we have for the

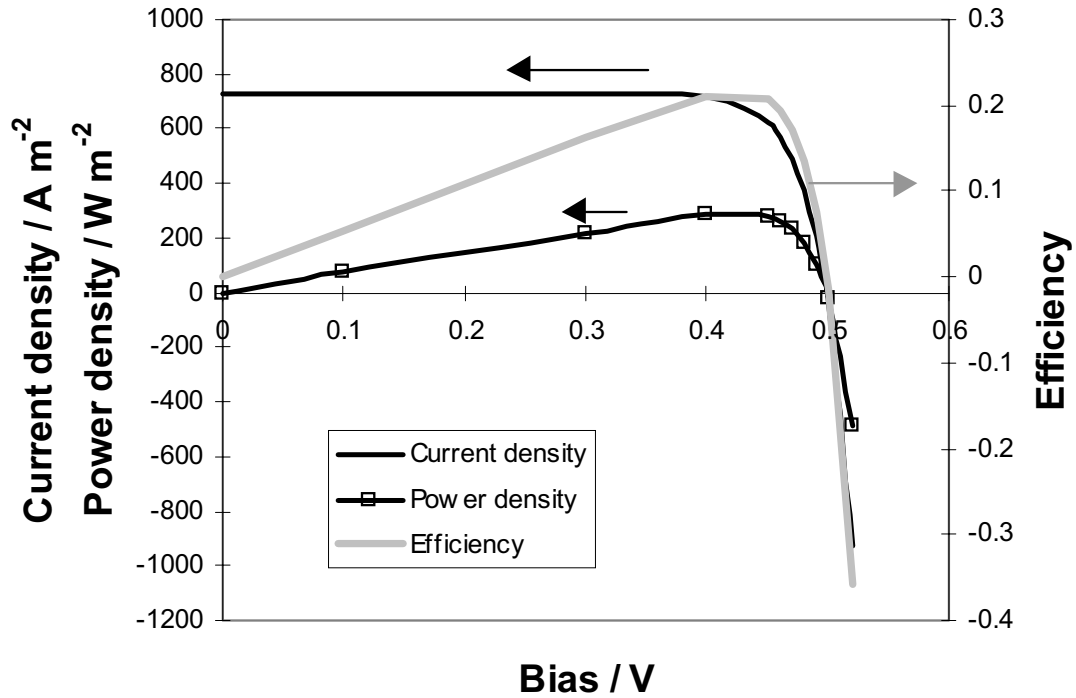
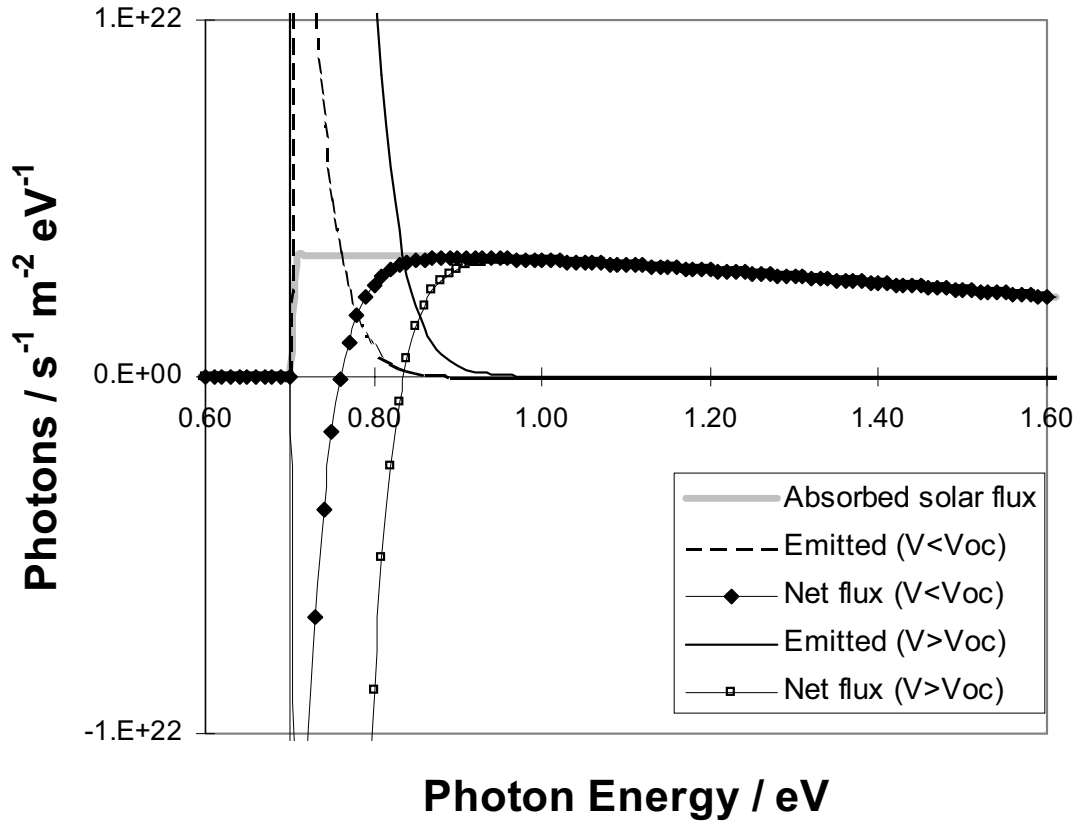


Fig. 2.7. (a) Absorbed ( $b_s(E)$ ), emitted ( $b_e(E, qV)$ ) and net ( $= b_s - b_e$ ) spectral photon flux for a biased cell of  $E_g = 0.7$  V at 300 K illuminated by a black body sun at 5760 K. (b) Current density, power density and efficiency of the device in (a) as a function of  $V$ . The current is calculated from  $q$  times the integrated net photon flux.

extracted power density from Eq. 1.6

$$P = VJ(V)$$

with  $J(V)$  given by Eq. 2.24 above. The power conversion efficiency is

$$\eta = \frac{VJ(V)}{P_s}. \quad (2.26)$$

Maximum efficiency is achieved when

$$\frac{d}{dV}(J(V)V) = 0. \quad (2.27)$$

The bias at which this occurs is the maximum power bias,  $V_m$  introduced in Chapter 1. In Fig. 2.7(b) the output power density for a 0.7 eV band gap photoconverter in a black body sun is plotted as a function of bias. At the maximum,  $V_m = 0.45$  V, the power conversion efficiency is around 20%.

#### 2.5.4. *Effect of band gap*

Given all of the assumptions made above, the power conversion efficiency of the ideal two band photoconverter is a function only of  $E_g$  and the incident spectrum. If the incident spectrum is fixed, then  $\eta$  depends only on the band gap. Intuitively we can see that very small and very large band gaps will lead to poor photoconverters: in the first case because the working value of  $V$  is too small, ( $V_m$ , like  $V_{oc}$ , is always less than  $E_g$ ) and in the second because the photocurrent is too small. For any spectrum there is an optimum band gap at which  $\eta$  has a maximum. Figure 2.8 shows the variation of  $\eta$  with  $E_g$  calculated in this way for the standard AM1.5 solar

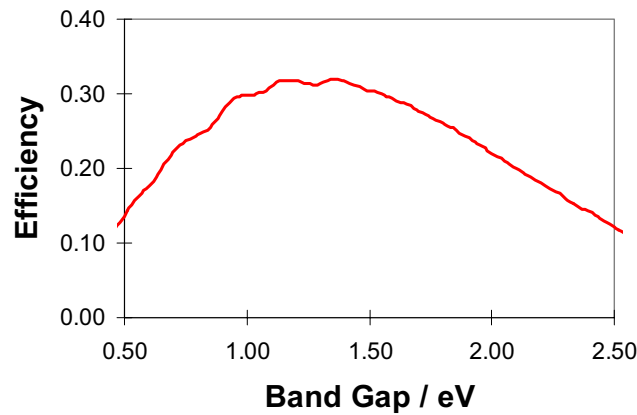


Fig. 2.8. Calculated limiting efficiency for a single band gap solar cell in AM 1.5.

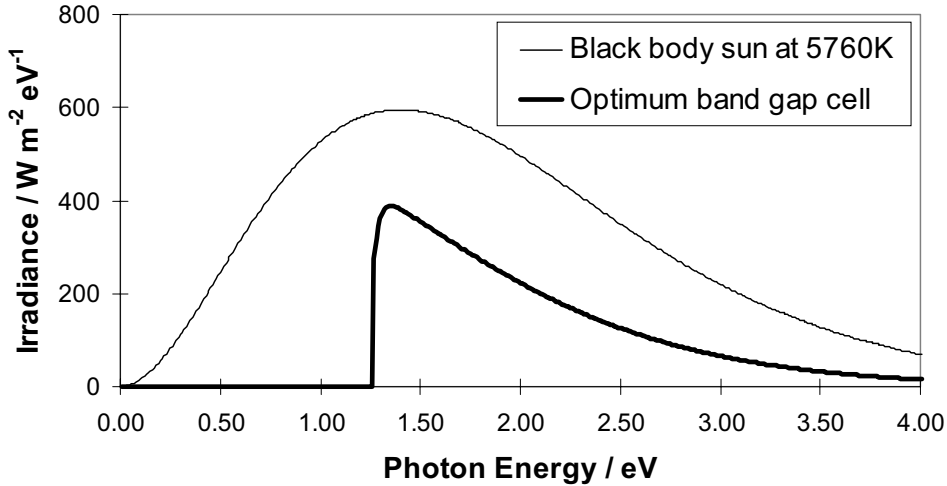


Fig. 2.9. Power spectrum of a black body sun at 5760 K, and power available to the optimum band gap cell.

spectrum. It has a maximum of about 33% at an  $E_g$  of around 1.4 eV. Optimising the performance of the ideal single band gap photoconverter is therefore a matter of choosing the right material.

In Fig. 2.9 the available power spectrum for an optimum band gap cell at maximum power point is compared with the incident power from a black body sun. Clearly, no photons with energy less than  $E_g$  contribute to the available power. Photons of  $E > E_g$  are absorbed but deliver only  $\Delta\mu (= qV_m)$  of electrical energy to the load, so only  $\Delta\mu/E$  of their power is available. The figure shows how this fraction falls as  $E$  increases. Even at  $E = E_g$  only a fraction  $\Delta\mu/E_g$  of the incident power is available, since  $qV_m < E_g$ .

### 2.5.5. Effect of spectrum on efficiency

To model the influences of spectrum on limiting efficiency, it is convenient to use a black body spectrum at  $T_s$  as the illuminating source. The spectrum of a 5760 K black body with the angular width of the sun is a good model of the extra-terrestrial (Air Mass 0) spectrum and predicts a limiting efficiency of around 31% at a band gap of 1.3 eV [Araujo, 1994], somewhat lower than the maximum efficiency in AM1.5.

If the spectrum is shifted to the red, by reducing the temperature of the source, the optimum band gap and the limiting efficiency are both reduced. Clearly, in the limit where  $T_s = T_a$  the cell is in equilibrium with the source and there is no net photoconversion. On the other hand, if the temperature of the source is increased relative to the cell, so is the photoconversion

efficiency. In the limit where  $T_a \rightarrow 0$ , the radiative current vanishes and bias has no effect on the net photocurrent. Then the optimum operating bias is  $V = E_g/q$  (anything higher is physically unreasonable) and if all carriers are collected with  $\Delta\mu = qV$  then the maximum efficiency is given by

$$\eta = \frac{E_g \int_{E_g}^{\infty} b_s(E) dE}{\int_0^{\infty} E b_s(E) dE} .$$

This has a maximum of around 44% at a band gap of 2.2 eV for a 6000 K black body sun, increasing to higher values and higher band gaps for hotter suns. This limit was reported by Shockley and Queisser [Shockley, 1961] as the ultimate efficiency of the solar cell. In practice the cooling of the cell below the ambient requires an input of energy which reduces the net efficiency.

Another way of improving the efficiency through the spectrum is to alter the angular width of the sun. Recall from Eq. 2.2 that the solar flux contains a factor  $F_s$  which represents the solid angle subtended by the sun. If this angle is increased by *concentrating* the light, the net photocurrent will increase and the first term (absorbed flux) in the integrand in Eq. 2.24 will increase relative to the second (emitted flux). One way of looking at this is to consider that while the cell emits radiation in all directions, it absorbs sunlight only from a small angular range. Increasing the angular range improves the balance, as does restricting the angular range for emission. This will be considered in more detail in Chapter 9. Optimising the power density then yields a new  $\eta(E_g)$  curve with a higher maximum at a smaller band gap. For light which is concentrated by a factor of 1000, a limiting efficiency of about 37% at  $E_g = 1.1$  eV is predicted [Henry, 1980]. For a concentration factor of  $4.6 \times 10^4$  (the maximum)  $\eta$  is over 40%. However, these estimates ignore the practical effect that under high concentrations the cell will be heated, and emit more strongly.

## 2.6. Requirements for the Ideal Photoconverter

In the above we made the following assumptions:

- that our photovoltaic material has an energy gap which separates states which are normally full from states which are normally empty;
- that all incident light with  $E > E_g$  is absorbed;
- that each absorbed photon generates exactly one electron-hole pair;

- that excited charges do not recombine except radiatively, as required by detailed balance;
- that excited charges are completely separated;
- that charge is transported to the external circuit without loss.

Let's examine what these assumptions mean for real physical systems.

### ***Energy gap***

Many solid state and molecular materials satisfy the condition of the energy or band gap. The need for conductivity make semiconductors particularly suitable. With band gaps in the range 0.5–3 eV semiconductors can absorb visible photons to excite electrons across the band gap, where they may be collected. The III–V compound semiconductors gallium arsenide (GaAs) and indium phosphide (InP) have band gaps close to the optimum (1.42 eV and 1.35 eV, respectively, at 300 K) and are favoured for high efficiency cells. The most popular solar cell material, silicon, has a less favourable band gap (1.1 eV, maximum efficiency of 29%) but is cheap and abundant compared to these III–V materials. Other compound semiconductors, in particular cadmium telluride (CdTe) and copper indium gallium selenide (CuInGaSe<sub>2</sub>) are being developed for thin film photovoltaics. Recent developments in semiconducting molecular materials indicate that organic semiconductors are promising materials for photovoltaic energy conversion in the future.

### ***Light absorption***

High absorption of light with  $E > E_g$  is straightforward to achieve in principle. Increasing the thickness of the absorbing layer increases its optical depth, and for most semiconductors almost perfect absorption can be achieved with a layer a few tens or hundreds of microns thick. However, the requirements of high optical depth *and* perfect charge collection, make very high demands of material quality.

### ***Charge separation***

For a current to be delivered, the material should be contacted in such a way that the promoted electrons experience a spatial *asymmetry*, which drives them away from the point of promotion. This can be an electric field, or a gradient in electron density.

This asymmetry can be provided by preparing a *junction* at or beneath the surface. The junction may be an interface between two electronically different materials or between layers of the same material treated in different ways. It is normally large in area to maximise the amount of solar energy intercepted. For *efficient* photovoltaic conversion the junction quality is of central importance since electrons should lose as little as possible of their electrical potential energy while being pulled away. In practice preparing this large area junction successfully and without detriment to material quality is a challenge and limits the number of suitable materials.

### ***Lossless transport***

To conduct the charge to the external circuit the material should be a good electrical conductor. Perfect conduction means that carriers must not recombine with defects or impurities, and should not give up energy to the medium. There should be no resistive loss (no series resistance) or current leakage (parallel resistance). The material around the junction should be highly conducting and make good Ohmic contacts to the external circuit.

Mechanisms for excitation, charge separation and transport can be provided by the semiconductor  $p$ - $n$  junction, which is the classical model of a solar cell. In this system charge separation is achieved by a charged junction between layers of semiconductor of different electronic properties: *i.e.*, the driving force which separates the charges is electrostatic. The  $p$ - $n$  junction will be treated in detail in Chapter 6.

### ***Optimum load resistance***

Finally, the load resistance should be chosen to match the operating point of the cell. As we have seen above, individual solar cells tends to offer photovoltages of less than one volt which are often too small to be useful. For most applications, voltage is increased by connecting several cells in series into a module, and sometimes by connecting modules in series and parallel into a larger array. In practice the load resistance should be matched with the maximum power point of the array, rather than the cell.

As a consequence of the demands on the material, only a very small number of materials, all of them inorganic semiconductors, have been developed for photovoltaics. Only a few of the many potentially useful materials have the necessary technological history. The favourites are those developed for the microelectronics industry — silicon, gallium arsenide,

amorphous silicon, some II–VI and other III–V compounds. It is only recently that materials have been developed *primarily* for their application in photovoltaics.

In terms of the above discussion, the main reasons why real solar cells do not achieve ideal performance are these:

- Incomplete absorption of the incident light. Photons are reflected from the front surface or from the contacts or pass through the cell without being absorbed. This reduces the photocurrent.
- Non-radiative recombination of photogenerated carriers. Excited charges are trapped at defect sites and subsequently recombine before being collected. This can occur at the surfaces where the defect density is higher, or near interfaces with another material, or near the junction. Recombination reduces both the photocurrent, through the probability of carrier collection, and the voltage, by increasing the dark current.
- Voltage drop due to series resistance between the point of photogeneration and the external circuit. This reduces the available power, as discussed in Chapter 1. It also means that  $\Delta\mu \neq qV$ .

In following chapters we shall see how far different designs and materials meet the demands of the ideal photovoltaic converter.

## 2.7. Summary

The sun emits radiant energy over a range of wavelengths, peaking in the visible. Its spectrum is similar to that of a black body at 5760 K, although it is influenced by atmospheric absorption and the position of the sun. The standard solar spectrum for photovoltaic calibration is the AM 1.5 spectrum.

A photovoltaic solar energy converter absorbs photons of radiant energy to excite electrons to a higher energy level, where they have increased electrochemical potential energy. In order for these excited electrons to be extracted as electrical power, the material must possess an energy gap or band gap. To calculate the absolute limiting efficiency of a photovoltaic energy converter, we use the principle of detailed balance. This allows for the fact that any body which absorbs light must also emit light. A photovoltaic device will emit more light when optically excited on account of the extra electrochemical potential energy of the electrons. This radiative recombination is the mechanism which ultimately limits the efficiency of a photovoltaic cell. The current delivered by the ideal photoconverter is due

to the difference between the flux of photons absorbed from the sun and the flux of photons emitted by the excited device, while the voltage is due to the electrochemical potential energy of the excited electrons. From this we calculate the current–voltage characteristic of an ideal solar cell. The maximum efficiency depends upon the incident spectrum and the band gap, and for a standard solar spectrum it is around 33% at a band gap of 1.4 eV. For a real device to approach the limiting efficiency, it should have an optimum energy gap, strong light absorption, efficient charge separation and charge transport, and the load resistance should be optimised.

## References

- G.L. Araujo and A. Marti, “Absolute limiting efficiencies for photovoltaic energy conversion”, *Solar Energy Materials and Solar Cells* **33**, 213 (1994).
- A. de Vos, *Endoreversible Thermodynamics of Solar Energy Conversion* (Oxford University Press, 1992).
- R. Gottschalg, *The Solar Resource and the Fundamentals of Radiation for Renewable Energy Systems* (Sci-Notes, Oxford, 2001).
- C.H. Henry, “Limiting efficiencies of ideal single and multiple energy gap terrestrial solar cells”, *J. Appl. Phys.* **51**, 4494–4499 (1980).
- W. Shockley and H.J. Queisser, “Detailed balance limit of efficiency of  $p$ – $n$  junction solar cells”, *J. Appl. Phys.* **32**, 510–519 (1961).
- P. Wurfel, “The chemical potential of radiation”, *J. Phys.* **C15**, 3697 (1982).