The Probable Solution-Solar Energy

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Chapter 1

Introduction

One of the major concerns that will face humanity in the next century is energy demands. Today, in order to meet the earths insatiable energy needs, fossil fuels (coal, oil, and natural gas) are being combusted at an accelerated rate and the effect on the earth and its environment is an adverse one. What does this mean? It means that there are two major problems that need to be addressed politically, economically and technologically. The first problem with fossil fuels are that they are considered ‘non-renewable’. By definition, they are formed from decayed plants and animals that have been converted to crude oil, coal, natural gas, or heavy oils thought by exposure to heat and pressure in the earth’s crust over hundreds of millions of years. Hence the term ‘non-renewable’ is appropriate because use is faster then replenishment, years compared to millions of years. The second problem that must be addressed is a by product of the first, pollution. The products of combustion from fossil fuels, oxides of nitrogen (NO_x), volatile organic compounds (VOC’s), particulate matter (PM), Sulfur dioxide (SO_2), etc., are thought to contribute not only to individual health problems but to Global Warming which will have devastating effects on the planet and its inhabitants.

So what are the possible solutions to meet the unavoidable energy crisis this planet faces. For starters, it begins with renewable energy, which is energy obtained from sources that are essentially inexhaustible. They include wind, geothermal, photovoltaic, waste, wood, etc. Each have their own advantages and disadvantages that need to be weighted based on their potential impact on the planet and society.

It probably comes as a surprise to all that in only a few days the earth receives more energy from the sun then all the fossil fuel burnt in history.

Table 1.1: **Examples of Energy Sources**

Energy Source	Classified as
Oil Natural Gas Coal Fission	Non-renewable
Solar Biomass Wind Geothermal Hydropower	Renewable

As it is, the sun in one way or another is the source of all energy on this planet. If a tiny fraction of the sun's energy could be tapped, then all our energy needs could be satisfied. Probably the easiest way to do this is to convert the sunlight directly into electricity. This can be achieved through solar or photovoltaic cells, which operate on the principals of solid state physics. Basically, the cell operates as a battery that can last as long as the sun does (in principal). This approach would eliminate the pollution problem associated with fuels and would be 'perpetual' in the sense that as long as the sun is around, energy would be readily available. Today, these devices are available but costs more to produce electricity then burning fuels. If material cost could decrease and efficiency could improve, along with a bit of engineering, then they would be a big player in terms of supplying the world's energy.

This paper is about these photovoltaic devices and is organized into two parts, the physics behind these devices where the basic principals are explored along with some new concepts to improve cell design. While the other part deals with the feasability of solar energy and what impact it will have.

1.1 The Problem

The problem, as mentioned in the introduction, is very obvious even though many have turned a blind eye. Fossil fuels will eventually be 'extinct' to meet our hungry appetite for energy and along the way pollute the planet with its products of combustion. This is a very real problem that cannot be ignored.

In 1980[1], the worlds annual energy production was 287.559 quadrillion British Thermal Units (BTU's) with ≈ 90% produced from fossil fuels. In 2004, the worlds annual energy production was 443.1 quadrillion BTU's with ≈ 86% produced from fossil fuels. These are very alarming numbers because in approximately a quarter century, our energy production has grown 54% and our dependance on fossil fuels has been relatively the same.

Burning these fuels has environmental and social costs with the consequences well documented, some are listed below;

- Ground-level ozone or smog
- Acid rain
- Human health issues which include aggravating asthma, heart disease, inflame and damage cells that line your lungs, reduce lung function, irritate your respiratory system, irregular heartbeats, etc.
- Global warming

It is an understatement to say that there needs to be a solution and fast.

1.2 Probable Solution

In 2004, the total energy produced on earth was 467×10^{18}joules. The possible non-renewable solutions listed in table 1.1 should have the potential to produce at least this annual amount of energy, while having a non-negative environmental impact on the planet. Ultimately, converting solar to electrical energy has the most potential in terms of providing the necessary energy while being 'environmental friendly'.

Solar energy is a one-step conversion from light to electricity using cells to absorb the light emitted from the sun. Energy used in this manner is non-polluting with the only side-effect of redistributing energy from one location to another. It will become truly mainstream when the cost per watt is comparable to the other forms of energy. At the moment it is about four times as expensive but increased concerns over fuel supply and pollution have encouraged government and concerned environmentalists to become increasingly prepared to offset the cost.

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[1] Energy Information Administration, official energy statistics from the U.S. Government

Part I

Physics of Solar Energy

Chapter 2

Introduction

The principals used in solar photovoltaic energy are based on the quantum mechanicals of light and solids. Light energy comes in the form of light packets called photons at a certain frequency or wavelength, which is related to its energy by the equation

$$E = hf = \frac{hc}{\lambda}$$

where, h is planks constant, f is frequency, c is the speed of light, and λ is wavelength. If this energy of the photon is sufficient enough to excite an electron from the valence band, across the band gap in a semi-conductor, to the conduction band then it is free to move. This creates what is called an 'electron-hole' pair, with the electron in the conduction band able to travel and transport energy and the hole (vacancy that is left behind from the electron) behaving similar to the electron (opposite charge, wavevector, and energy to the missing electron). Normally, when electrons are excited in solids they relax back down to their ground state very quickly and no useful work can be extracted. However, in a semi-conductor the electrons will relax to the edge of the conduction band on the order of femtoseconds ($10^{-15}s$) but the next step, which is to relax back down across the band gap to the valence band, happens on the order of microseconds ($10^{-6}s$). In a photovoltaic device an asymmetry is built in so that the excited electrons are pulled away to an external circuit before they can relax. This extra energy creates a potential difference and this drives the electrons through a load in the circuit to do electrical work.

In this chapter, the basics of solar cells are presented while some important properties of these devices are explored. The properties that define these devices are the efficiency η, photocurrent density J_{sc}, quantum efficiency QE, dark current density J_{dark}, open circuit voltage V_{oc}, parasitic resistances, and non-ideal diode behavior.

2.1 A simple device

The solar cell is the basic building block of a photovoltaic device and is a two terminal device which behaves like a diode (a component that restricts the direction of flow of charge carriers. Essentially, it allows an electric current to flow in one direction, but blocks it in the opposite direction) in the dark and generates a photovoltage when illuminated by the sun. A very simple device is made of a semi-conductor normally 100m^2 in area. On the surface is an anti-reflecting coating so that as much visible light is absorbed as possible. Metal contacts are imprinted on the surface to make electrical contact.

The very basic unit generates a very small dc photovoltage between 0.5 to 1.0 volts (V) and a photocurrent density (in short circuit) of tens of milliamps per cm^2. The voltage of one cell isn't enough to produce anything worth while, therefore cells are connected in series called *modules*. These modules using consist of between 28 and 36 cells to produce a dc output voltage of 12 V under normal illumination conditions. Some applications require a larger current and voltage output and if this is the case then modules are connected in series or parallel array (photovoltaic generator) to meet the design specifications. The cells within a module have blocking diodes so that if one would malfunction or failed then there wouldn't be complete power loss. The photovoltaic generator is normally in multiples of 12 V, however for a normal application it is accompanied with a battery which stores the charge because illumination is variable. In order to get ac electrical power, the dc current supplied by the modules is converted using what is called an inverter.

2.2 Properties and definitions

Before the physics of a photovoltaic device is discussed, it is only natural to introduce some important definitions and/or properties. When the cell is illuminated, a voltage is developed and when the terminals are isolated this voltage is called the open circuit voltage or V_{oc} (normally measured in volts V). The current that is drawn when the two terminals are connected together is called the short-circuit current I_{sc} (normally measured in mA). When there is an intermediate load resistance R_L, the voltage is between 0 and

V_{oc} and delivers the current $V = IR_L$. The current $I(V)$ is determined by the current-voltage characteristic of the cell under illumination. Sometimes the short circuit current-density J_{sc} is used since the current is proportional to the lighted area. The next few sections will develop these concepts that have been introduced up to this point.

2.2.1 Photocurrent

The photocurrent that is generated from the cell is dependent on the incident light and to relate the incident light to the current density J_{sc} we need the quantum efficiency or (QE). The quantum efficiency is the probability that an incident photon of energy E will deliver one electron to the external circuit. It is dependent on the solar cell material, the efficiency of charge separation, and the efficiency of charge collection in the device. Current-density is then

$$J_{sc} = q \int b_s QE(E) dE \tag{2.1}$$

and b_s is the incident spectral photon flux density (number of photons of energy in the range E to $E + dE$) which are incident on unit area per in unit time. It is important to note that QE and photon flux can be given in functions of photon energy, hence wavelength.

2.2.2 Dark current and open circuit voltage

A potential difference develops between the terminals when a load is present, which generates a current that acts in the opposite direction of the photocurrent. Obviously, the net current is reduced from the short circuit value. This reverse current is normally referred to as the dark current I_{dark}. Alot of the solar cells behave like diode in the dark, therefore the dark current is greater at forward bias ($V > 0$) then at reverse bias ($V < 0$). For an ideal diode the dark current density is

$$J_{dark}(V) = J_o(e^{qV/k_B T} - 1) \tag{2.2}$$

and J_o is a constant, k_B is Boltzmann's constant, and T is Temperature in degrees Kelvin.

The current voltage characteristic can be well approximated as a superposition between the short circuit current and the dark current. However, the reverse current that occurs in the cell in response to voltage from illumination is not equal to the current which flows in the dark, it is a good approximation for most photovoltaic materials (will be used throughout this paper). Also it must be noted that the sign convention for photocurrent in photovoltaics is positive and with this along with the superposition approximation, the current density in the cell becomes

$$J(V) = J_{sc} - J_{dark}(V) \tag{2.3}$$

and for an ideal diode

$$J(V) = J_{sc} - J_o(e^{qV/k_BT} - 1) \tag{2.4}$$

Now when the dark current is equivalent to the short circuit photocurrent, the maximum voltage or V_{oc} can be found. This is equivalent to when the terminals are isolated. Using the above equations the open circuit voltage is found to be

$$V_{oc} = \frac{kT}{q} ln \left(\frac{J_{sc}}{J_o} + 1 \right) \tag{2.5}$$

this shows that as the light intensity increases, V_{oc} increases logarithmically (when $V > 0$, forward bias).

2.2.3 Efficiency

One of the most important characteristics of the solar cell is how efficient it is. Efficiency η of the cell is defined as the power density delivered as a fraction of the incident light spectrum power density P_s or

$$\eta = \frac{J_m V_m}{P_s} \tag{2.6}$$

with the cell power density being given by the familiar expression $P = JV$. The power density reaches a maximum at some point when V is between 0 and V_{oc}, and is V_m with a current density J_m. There is an important ratio that is also used in solar cell performance and it is called the fill factor defined as

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \tag{2.7}$$

which describes the 'squareness' of the $J - V$ curve. Now efficiency can also be related through the fill factor by

$$\eta = \frac{J_{sc} V_{oc} FF}{P_s} \tag{2.8}$$

These four quantities, FF, η, J_{sc}, V_{oc} are key performance characteristics in solar cell design.

2.2.4 Parasitic resistances

Power is dissipated throughout a solar cell device, more specifically through the resistance of the contacts and through leakage currents along the edges of the PV device. These effects electrically mimic two parasitic resistances in series (R_s) and in parallel (R_{sh}). As one can imagine, the series resistance occurs from the resistance of the cells material to current flow from the front surface contacts and resistive contacts. The parallel resistance occurs from leakage of current throughout the cell, around the edges of the device. When these resistances are included, the current density of the cell becomes

$$J(V) = J_{sc} - J_o(e^{q(V+JAR_s)/k_BT} - 1) - \frac{V + JAR_s}{R_{sh}} \tag{2.9}$$

One can observe that it is optimum to have very large parallel resistances and very small series resistances.

Chapter 3

Principals-Light Energy to Electricity

3.1 Introduction

In the first chapter, the solar cell was introduced along with the important characteristics that defined its performance. This chapter will introduce the source and how much power can be expected from it, how much work is available, the entropy limitations, and discuss an ideal photovoltaic converter.

3.2 The Source

The source for a photovoltaic converter is the sun, therefore it is important to discuss its physical properties. The sun is essentially a sphere of gas heated by nuclear fusion reaction at its center. Electromagnetic radiation is emitted with a wavelength determined by the hot body's temperature. The term 'black body' is a mathematical ideal that is a perfect absorber of light and therefore a perfect emitter. Although it is an ideal many physical objects, included the sun, can be modeled as a black body. The number of photons that are emitted at a point **s** on the surface of a black body in the energy range E to $E+dE$, called the spectral photon flux $\beta_s(E, s, \theta, \phi)$, unit area per unit solid angle per unit time, is

$$\beta_s(E, s, \theta, \phi) d\Omega ds dE = \frac{2}{h^3 c^2} \left(\frac{E^2}{e^{\frac{E}{kT_s}} - 1} \right) d\Omega ds dE \tag{3.1}$$

where ds is the element surface area around s and $d\Omega$ is the unit of solid angle around the direction of emission of the light. This indicates that as the body is heated the total energy of the radiation increases and the frequency increases (when metal is heated it glows red, then yellow as it gets hotter). The flux normal to the surface is given integrating over unit solid angle and resolved around ds,

$$\begin{aligned} b_s(E,s)dsdE &= \int_\Omega \beta_s(E,s,\theta,\phi)cos\theta d\Omega dsdE \\ b_s(E,s)dsdE &= \frac{2F_s}{h^3c^2}\left(\frac{E^2}{e^{\frac{E}{kT_s}}-1}\right)dsdE \end{aligned} \tag{3.2}$$

and F_s is a geometrical factor which is an artifact from the integration. At the surface of a black body this range is a hemisphere and the geometrical factor is π, away from the surface the factor is reduced to $\pi sin^2\theta_{sun}$. The angle, θ_{sun}, is the half angle subtended by the black body to the point where the flux is measured. For the sun as seen from earth, $\theta_{sun} = 0.26°$, (corresponding to a reduced F_s of 4.6×10^4) and if the temperature at all points **s** on the surface of the black body are equivalent, then equation 3.2 is

$$b_s(E) = \frac{2F_s}{h^3c^2}\left(\frac{E^2}{e^{\frac{E}{kT_s}}-1}\right) \tag{3.3}$$

Now the emitted energy flux density or solar irradiance is given by $Eb_s(E)$ and integrating over E gives the total emitted power density which is $\sigma_s T_s^4$. Stefan's constant σ_s is given by

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

this shows that at the surface of the sun, using $T_s = 5760K$, a power density of 62MWm^{-2}. Therefore, using the reduced factor of 4.6×10^4 gives the total power density of $1353\ \text{Wm}^{-2}$ at the earths surface.

When the sunlight hits the earth's atmosphere it is attenuated by Rayleigh scattering, dust particles, and absorption by the atmosphere and its gases. Attenuation is highly variable but the most important parameter is the light path length through the atmosphere. The shortest distance being when the sun is directly overhead and the ratio of any other distance to this minimum is called the optical air mass (AM). The standard is defined as AM1.5 and the corresponding irradiance is $1000\ \text{Wm}^{-2}$. Obviously this number fluctuates depending on the position of the sun, earth and condition of the sky.

Before moving on, one more important characteristic from the sun's light must be developed. As opposed to directional, sunlight that hits the earth's atmosphere and scatters so that some is incident on terrestrial cells from all directions is called diffuse light. As such a system that only converts the direct component of the sun can waste a lot of energy. A system that can convert both the direct and diffuse light from the sun is a non-concentrating system and doesn't have to track the sun (most direct systems track the sun). The overall efficiency of such a system would then be

$$\eta = f_{dir}\eta_{dir} + (1 - f_{dir})\eta_{diff} \tag{3.4}$$

where f_{dir} is the fraction of light that is direct, η_{dir} is the conversion efficiency for this light, and η_{diff} is the conversion efficiency for diffuse light. For a normal concentrating system $\eta_{diff} = 0$ but for a normal non-concentrating system $\eta_{diff} \approx \eta$. Normally, $\eta_{dir} > \eta_{diff}$ due to the performance gains possible by taking advantage of light collimation.

3.3 Entropy Limitations

At this point, it is important and necessary to lay out the thermodynamic's for a photovoltaic device. Later on, these will be developed for more specific devices or systems of devices. The goal is to figure out the upper most thermodynamic limit for a photovoltaic device so an efficiency comparison can be made.

When there is energy exchange, there will always be some sort of non-negative entropy production and both can expressed as conservation laws. In solar conversion, we are interested in steady-state conditions and equilibrium between energy fluxes. Associated with an energy transfer as heat at a rate $\dot{E}$ to or from a body with temperature T is the entropy flux, $\dot{S} = \dot{E}/T$, if the transfer occurs in the presence of an infinitesimally small temperature differential. There is additional entropy generation if temperature gradients are involved.

3.3.1 General Efficiency Limit

The general efficiency limit for a photovoltaic system is the Carnot limit. The inputs from the sun are $\dot{E}_s$ and $\dot{S}_s = \dot{E}_s/T_s$, where T_s is the temperature of the suns photosphere (using $5760K$). The outputs are the useful work or $\dot{W}$, with zero entropy flux and heat flux or $\dot{Q}$ into the ambient, with entropy flux associated as $\dot{S}_a = \dot{Q}/T_a$ (T_a being the ambiet temperature which is assumed to be $300K$). There is also one more input which is the entropy generation flux $\dot{S}_g$ associated with the photovoltaic conversion process. Depending on the process, this number can be very large. Now, using the the first and second law of thermodynamics we see that the two resulting equations are found;

$$\dot{E}_s = \dot{W} + \dot{Q} \tag{3.5}$$

$$\dot{S}_s + \dot{S}_g = \frac{\dot{Q}}{T_a} \tag{3.6}$$

These two equations, linked by $\dot{Q}$, can put put into the more compact form

$$\dot{E}_s = \dot{W} + T_a(\dot{S}_s + \dot{S}_g) \tag{3.7}$$

Then the conversion efficiency is obviously $\eta = \dot{W}/\dot{E}$ or

$$\eta = (1 - \frac{T_a}{T_s}) - \frac{T_a \dot{S}_g}{\dot{E}_s} \tag{3.8}$$

if the entropy generation is zero or $\dot{S}_g = 0$ then the maximum efficiency is $\approx 95\%$. The intresting feature about this derivation is that nothing is said about the converter, only that there is zero entropy generation during the process. Since this is the main requirement, zero entropy generation, that means that there can be no generation during transmission, absorption or converting the sunlight into useful work. This is very hard to imagine, therefore another efficiency called the Landsberg limit is a more 'realistic' limit.

3.3.2 Landsberg Limit

A more realistic limit or process is when a system has additional outputs from the converter. They are $\dot{E}_c$, which is the energy that is re-radiated from the converter and $\dot{S}_c$, the associated entropy flux associated with the energy re-radiation. Using similar analysis as before, we get the two equations;

$$\dot{E}_s = \dot{W} + \dot{Q} + \dot{E}_c \tag{3.9}$$

$$\dot{S}_s + \dot{S}_g = \frac{\dot{Q}}{T_a} + \dot{S}_c \tag{3.10}$$

and once again both have $\dot{Q}$ in common, therefore combining;

$$\dot{E}_s = \dot{W} + \dot{E}_c + T_a(\dot{S}_s + \dot{S}_g - \dot{S}_c) \tag{3.11}$$

with the efficiency being;

$$\eta = 1 - \frac{\dot{E}_c}{\dot{E}_s} - \frac{T_a \dot{S}_s}{\dot{E}_s} - \frac{T_a \dot{S}_q}{\dot{E}_s} + \frac{T_a \dot{S}_c}{\dot{E}_s}$$

or

$$\eta = (1 - \frac{T_a \dot{S}_s}{\dot{E}_s}) - (1 - \frac{T_a \dot{S}_c}{\dot{E}_c}) \frac{\dot{E}_c}{\dot{E}_s} - \frac{T_a \dot{S}_g}{\dot{E}_s} \tag{3.12}$$

however, now we are dealing with the total radiant energy from the sun instead of the net heat flux. The entropy flux of the sun is increased to $\frac{4}{3}\dot{E}_s/T_s$ and if the converter is considered a black-body at temperature T_c we get the efficiency

$$\eta = (1 - \frac{4T_a}{3T_s}) - (1 - \frac{4T_a}{3T_c}) \frac{T_c^4}{T_s^4} - \frac{T_a \dot{S}_g}{\dot{E}_s} \tag{3.13}$$

where the T^4 terms come from the black body emission properties (σT^4). Once again if it is assumed that the entropy generation is zero then we get a maximum efficiency when $T_c = T_a$ of 93%. This is the upper most limit in solar energy conversion, however it has been claimed that this limit is impossible to obtain due to unavoidable entropy production during light absorption. Even though this limit has been derived for a very specific set of conversion assumptions, it is a very general solar energy conversion efficiency.

3.4 Absorption and Emission of Photons

It is very important to understand the absorption and emission process of photons in a photovoltaic device in equilibrium and when illuminated. In this section we will develop the basics of these processes under the two conditions. The assumption that the ambient performs like a black body is used.

3.4.1 In the Dark or Equilibrium

When the cell is in the dark, or in equilibrium, the ambient radiates at a temperature T_a. Assuming the black body spectral flux and integrating equation 3.3 over all directions, the incident flux of thermal photons normal to the surface of a flat plate solar cell is

$$b_a(E) = \frac{2F_a}{h^3 c^2} \left(\frac{E^2}{e^{\frac{E}{kT_a}} - 1} \right) \tag{3.14}$$

and once again F_a is the geometrical factor equal to π (assume received over a hemisphere). Then if we assume that each photon of energy E generates a single electron then the current density absorbed is

$$j_{abs}(E) = q(1 - R(E))a(E)b_a(E) \tag{3.15}$$

where $a(E)$ is the probability that a photon of energy E will be absorbed (it is known as the absorbance and is determined by the absorption coefficient of the material), $R(E)$ is the probability of reflection. In order to obtain the total current, then equation 3.15 should be integrated over the surface of the cell. This result depends on the interface of the rear surface.

The cell can also emit photons by two processes, spontaneous and stimulated emission. We are going to neglect stimulated emission for now because the conduction band is almost empty. Spontaneous emission occurs when the electron releases its potential energy from the conduction band back down to the valence band in the form of a photon. This happens to maintain steady-state conditions. If the probability of emission of a photon is called emissivity or just ϵ, then the current density is

$$j_{rad}(E) = q(1 - R(E))\epsilon(E)b_a(E) \tag{3.16}$$

and in order to maintain steady-state conditions one can observe that the two current densities must balance or $a(E) = \epsilon(E)$. In quantum mechanics, this is the result of the matrix element for optical transitions from the ground to the excited and excited to ground must be identical.

3.4.2 Illumination of the Solar Cell

Since the solar cell is now under illumination, it absorbs solar photons of energy E at the rate (similar form as in the previous subsection)

$$(1 - R(E))a(E)b_s(E) \tag{3.17}$$

and the equivalent absorbed current density is given by

$$j_{abs}(E) = q(1 - R(E))a(E)\left(b_s(E) + \left(1 - \frac{F_s}{F_e}\right)b_a(E)\right) \tag{3.18}$$

and b_a is introduced to allow for the fraction of ambient flux that has been replaced by solar flux. Now the excited electrons population has raised as a result of the illumination, which results in the electrochemical potential energy being raised $\Delta\mu > 0$. Now, as one can imagine, spontaneous emission has increased and depends on this $\Delta\mu$. I am just going to state here and not derive a more general version of Planck's radiation law and when integrated over the range of solid angle through which the photons can escape, the photon flux emitted normal to the surface is,

$$b_e(E, \Delta\mu) = \frac{2F_e n_s^2}{h^3 c^2} \left(\frac{E^2}{e^{\frac{E-\Delta\mu}{kT_a}} - 1} \right) \tag{3.19}$$

and $F_e = \pi sin^2\theta_c$, where θ_c being the critical angle derived from snell's law. Therefore, $F_e = \pi\frac{n_o^2}{n_s^2}$ with n_o being the surrounded medium. At the surface, the index of refraction $n_o = 1$ which is that of air. Now, $F_e n_s^2$ can be replaced by F_a remembering that this value is equal to π.

$$b_e(E, \Delta\mu) = \frac{2F_a}{h^3 c^2} \left(\frac{E^2}{e^{\frac{E-\Delta\mu}{kT_a}} - 1} \right) \tag{3.20}$$

Getting back to the current density for photon emission, which is just

$$j_{rad}(E) = q(1 - R(E))\epsilon(E) b_e(E, \Delta\mu) \tag{3.21}$$

Noting that $\epsilon(E) = a(E)$ still holds when $\Delta\mu$ is constant throughout the device, the net current density is just $j_{abs} - j_{rad}$ resulting in

$$j_{net} = q(1 - R(E))a(E) \left(b_s(E) + \left(1 + \frac{F_s}{F_a}\right) b_a(E) - b_e(E, \Delta\mu) \right) \tag{3.22}$$

3.5 Available Work

In this section, only the available work for a two-level system is considered in which the lower band is initially full and the upper band (excited) is empty. Between these bands is the energy gap or E_g and photons that are less then this energy gap are not absorbed.

3.5.1 Photocurrent

Photocurrent is due to the net absorbed photon flux (excess of that from equilibrium) from the sun and since the angular range of the sun is small compared to the ambient, we can make the assumption that the term F_s/F_e is negligible. Also, if η_c is the probability that the electron will be collected the photocurrent density J_{sc} is just

$$J_{sc} = q \int_0^\infty \eta_c(E)(1 - R(E))a(E)b_s(E)dE \tag{3.23}$$

one can observe that this equation is the same as equation 2.1, where the quantum efficiency $QE(E) = \eta_c(E)(1 - R(E))a(E)$. Now we assume perfectly absorbing, non-reflective material and that all the incident light greater then the energy gap promotes one electron to the upper band. With perfect charge collection so the $\eta = 1$, we can say that the current density for the short circuit can be expressed entirely as a function of the energy gap so that

$$J_{sc} = q \int_{E_g}^{\infty} b_s(E) dE \tag{3.24}$$

This integral is a bit difficult to evaluate but it can be shown that the approximate solution is

$$J_{sc} = q \frac{2F_s (kT)^3}{h^3 c^2} \int_{\epsilon_g}^{\infty} \frac{\epsilon^2 d\epsilon}{e^{\epsilon} - 1} \tag{3.25}$$

$$J_{sc} = q \frac{2F_s (kT)^3}{h^3 c^2} \Gamma(3) \beta_2(0, \epsilon_g) \tag{3.26}$$

where $\epsilon_g = E_g/kT_s$ and Γ is just the Gamma function and $\beta_2(0, \epsilon_g)$ is

$$\begin{aligned} \beta_2(0, \epsilon_g) &= \frac{\epsilon_g^2 \beta_0(-\epsilon_g)}{2} + \epsilon_g \beta_1(-\epsilon_g) + \beta_2(-\epsilon_g) && (3.27) \\ \beta_j(\eta) &= e^{\eta} + \frac{e^{2\eta}}{2^{j+1}[1 - (\frac{2}{3})^{j+1} e^{\eta}]} && (3.28) \end{aligned}$$

3.5.2 Net Current Density

As previously discussed in chapter 2, the net current density is just equation 2.3 with the dark current being the current that flows through the photovoltaic device when a bias is applied in the dark. Also, we are assuming that the only recombination comes from spontaneous emission as mentioned previously. The dark current is given by integrating the net emission or

$$J_{dark}(\Delta\mu) = q \int (1 - R(E)) a(E) (b_e(E, \Delta\mu) - b_e(E, 0)) dE \tag{3.29}$$

and once again we have to assume that $\Delta\mu$ is constant throughout the surface and that $a(E) = \epsilon(E)$. Going further, an ideal material with lossless carrier transport $\Delta\mu$ can be assumed to be constant everywhere and then equal to qV (where V is the applied bias). The net current density is therefore,

$$J(V) = q \int_0^{\infty} (1 - R(E)) a(E) [b_s(E) - (b_e(E, qV) - b_e(E, 0))] dE \tag{3.30}$$

and using the approximation as we did in deriving equation 3.24 this can simplify to

$$J(V) = q \int_{E_g}^{\infty} [b_s(E) - (b_e(E, qV) - b_e(E, 0))] dE \tag{3.31}$$

Looking at this equation and noticing that there is a constant exponential term in $b_e(E, qV)$, one can argue that this has the form of the ideal diode equation 2.4. One remark about the net current density is that as V is increased, the net current density decreases and at V_{oc} the net current density is zero. Also note that V_{oc} must always be less then E_g/q.

3.5.3 Available Power

From the analysis above, with all the assumptions made, the power density $VJ(V)$ is shown to be only a function of the band gap E_g even though the integral equations are extremely ‘messy’. For a given energy gap, the maximum power can be found by differentiating $VJ(V)$ with respect to V and set it equal to 0.

3.6 An Ideal System

The assumptions that have been made up to this point have been for an ideal photovoltaic converter and to summarize;

- The material has an energy gap where all the electrons are initially in the lower band (valence) and the upper band (conduction) is entirely empty.
- All the incident light that is larger then the energy gap is absorbed.
- Each photon that is absorbed generates one electron-hole pair.
- The promoted electrons only recombine through spontaneous emission.
- The promoted electrons are completely separated.
- There is no loss in charge transportation to the external circuit.

Chapter 4

Basics of Semiconductors

4.1 Introduction

In chapter 3, the properties of sunlight and requirements for photovoltiac conversion were considered. We concluded that the material needs to have an energy gap between the initial occupied band (valence) and the final unoccupied band (conduction) which could absorb photons and be able to transport the charge to an external circuit. A band gap exists in insulators and semiconductors but the gap in insulators is much to large to absorb visible light. This is why in photovoltaic conversion, semiconducting material is used.

A band gap is important because as an electron-hole pair is created with the absorption of a photon, the promoted electron will relax to lower energy levels very quickly until it reaches the band gap. The relaxation time across the band gap is much greater then the relaxation time within the band (on the order of femtoseconds within the band gap as opposed to μ seconds across the band gap). This allows it to remain in the conduction band long enough for it to be exploited. 'Thermalisation' is the term used to describe this decay within the conduction band down to the edge of it. If there was no band gap but a continuum of energy levels, like a metal, the electron relaxes to quickly for it to be exploited.

In this chapter, the properties/principals of semi-conductors are introduced but not derived from fundamentals. It is to highlight the physics that are important to the design and operation of the photovoltaic device. Therefore the concepts of density of states, Fermi-Dirac distribution function, doping, equilibrium, and electron and hole currents are introduced.

4.2 Some Concepts

4.2.1 Energy Bands

Materials that are used in photovoltaic systems can be classified as crystal-like structures. Since crystals are orderly and a periodic arrangement of the atoms, it allows us to build up the crystal by repeatedly stacking small subsections. These subsections, called unit cells, contain all the useful information in the crystal. This unit cell can be exploited by using quantum mechanics and applying periodic boundary conditions to show some interesting features that electrons associated with the atoms experience. One of these features are energy gaps or forbidden energies not allowed for electrons.

Quantum mechanics tells us that isolated atoms have a set of well-defined discrete energy levels available for the associated electrons. However, as atoms are brought closer and closer together the original levels spread out into bands of allowed energy levels. Between these allowed levels are energy gaps that are forbidden to electrons. In order get insight on where these energy gaps occur one could apply one dimensional quantum mechanics to square-well potentials with periodic boundary conditions. An example of this is shown in the Appendix and the method used is described by Dr. Gilmore in *Elementary Quantum Mechanics in One Dimension.*

4.2.2 Fermi-Dirac Statistics

At low temperatures, electrons occupy the lowest possible energy states. Since electrons are fermions, then only each energy level or orbital can occupy at most two electrons (each with opposite spin). The energy of the topmost filled orbital at absolute zero is called the fermi energy E_F. When the temperature increases, some of the electrons gain energy in excess of the fermi energy level. Occupancy of an allowed electron state of any given energy E is given by a probability function that is called the Fermi-Dirac distribution function;

$$f(E, E_F, T) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \tag{4.1}$$

This function is unity up to the fermi energy near absolute zero but then as the temperature rises the function 'smears' out and there is a probability that states higher or lower then the fermi energy will be occupied.

A semiconductor is very similar to an insulator with the only difference being a narrower band gap. At low temperatures, the semiconductor will not conduct but at higher temperatures the the Fermi-Dirac function smears out and allows some occupied levels in the conduction band.

4.2.3 Electrons and Holes

When the electrons gain some kinetic energy from increasing temperature, they are able to break free and be excited into the conduction band. In the conduction band, they are able to travel and transport charge or energy. The vacancies left behind in the valence band, called holes, are also able to move and conduct as well. Holes can be regarded as particles with a positive charge. The higher the temperature, more electrons are able to break free and more holes are created. This results into a higher conductivity.

A semiconductor can also conduct if the material is exposed to light with energy greater then the band gap. An electron will absorb the photon and gain energy which allows it to 'jump' the band gap into the conduction band. Once again the free electron and hole created in this way allow for conductivity, and this is called photoconductivity (described in Chapter 2).

Conductivity can also be influenced by the deliberate addition of impurities. Impurities with different number of valence electrons can be added to the material and electrons or holes may be freed more easily. This increases the number of carriers in the conduction and valence bands. This process of adding impurities is called doping and is very important as will be clear a bit later.

4.2.4 Density of States

Just how many of allowed states per unit volume in a semiconductor are there? It is easy for energies corresponding to the forbidden gap, zero, but nonzero for energies in allowed bands. This can be very difficult but for energies near the edges of the allowed bands, the solution simplifies.

Each quantum state in a crystal is defined by a unique **k** value and we know that each **k** can support two electrons. It is also known that there are $(1/2\pi)^3$ **k** states per unit volume. Therefore the density of states per unit volume, N(k), is

$$N(k)d^3k = \frac{2}{(2\pi)^3} \tag{4.2}$$

and if near the band minimum the structure is isotropic then

$$N(k)d^3k = N(k) \times 4\pi k^2 dk \tag{4.3}$$

It is also much more desirable to know the density of states in terms of energy, so the energy in terms of **k** can be computed using the parabolic band approximation (conduction band minimum energy and valence band maximum energy)which is just

$$E(k) = E_{c0} + \frac{\hbar^2 \left|k - k_{c0}\right|^2}{2m_c^*} \tag{4.4}$$

$$E(k) = E_{v0} - \frac{\hbar^2 \left|k - k_{v0}\right|^2}{2m_v^*} \tag{4.5}$$

where $E(_{c0}) = E_c(k_{c0}), E(_{v0}) = E_v(k_{v0})$ and m_c^*, m_v^* are the effective mass's defined as

$$\frac{1}{m_c^*} = \frac{\partial^2 E_c(k)}{\hbar^2 \partial k^2} \tag{4.6}$$

$$\frac{1}{m_v^*} = -\frac{\partial^2 E_v(k)}{\hbar^2 \partial k^2} \tag{4.7}$$

Now the density of states becomes

$$N(E) = \frac{2}{(2\pi)^3} \times 4\pi k^2 \times \frac{dk}{dE} \tag{4.8}$$

and using equations 4.4 and 4.5 the density of states for the conduction band and valence band are respectively

$$N_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_c^*}{\hbar^2}\right)^{\frac{3}{2}} (E - E_{c0})^{\frac{3}{2}} \tag{4.9}$$

$$N_v(E) = \frac{1}{2\pi^2} \left(\frac{2m_v^*}{\hbar^2}\right)^{\frac{3}{2}} (E_{v0} - E)^{\frac{3}{2}} \tag{4.10}$$

4.2.5 Density of Electrons and Holes

Since the density of the allowed states and probability of the occupancy of those states is known, it is possible to find the energy distribution of electrons and holes. Most of the electrons in the conduction band and holes in the valence band are near the band edges, this can determined by the nature of Fermi-Dirac function. The total number of electrons in the conduction band per unit volume can be determined by the equation;

$$n = \int_{E_c}^{\infty} f(E) N(E) dE \tag{4.11}$$

but since E_c is much larger then E_F for the conduction band $f(E)$ can be approximated to

$$f(E) \approx e^{(E_F - E)/kT} \tag{4.12}$$

Now using this approximation, the integral can be found analytically with the final result being

$$\begin{aligned} n &= N_c e^{(E_F - E_c)/kT} \qquad (4.13) \\ N_c &= 2\left(\frac{m_c^* kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \end{aligned}$$

Similar analysis shows that the density of holes in the valence band is determined by the equation;

$$p = \int_{-\infty}^{E_v} (1 - f(E))N(E)dE \tag{4.14}$$

and using similar approximations

$$\begin{aligned} 1 - f(E) &\approx e^{(E - E_F)/kT} \qquad (4.15) \\ p &= N_v e^{(E_v - E_F)/kT} \qquad (4.16) \\ N_V &= 2\left(\frac{m_v^* kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \end{aligned}$$

The product np results in a very useful expression that is a property of the material and doesn't involve the Fermi energy. It is called the intrinsic carrier density n_i

$$n_i^2 = np = N_c N_v e^{-E_g/kt} \tag{4.17}$$

We have no where assumed that the value is intrinsic (perfect crystal containing no impurities) and the only assumption being that the Fermi level from the edge of the two bands is large compared to kT. Since the product of the electron and hole density is constant, an introduction of an impurity to increase n for example will decrease p. This is an important result as we shall see later.

In an intrinsic semiconductor at thermal equilibrium the number of holes will equal the number of electrons so;

$$n = p = n_i = 2\left(\frac{kT}{2\pi\hbar^2}\right)^{3/2} (m_c^* m_v^*)^{3/4} e^{-(E_g/kt)} \tag{4.18}$$

and when we set equation 4.13 equal to 4.16, the Fermi Energy can be solved for to find;

$$E_F = \frac{E_c + E_v}{2} + \frac{kT}{2} ln\left(\frac{N_v}{N_c}\right) \tag{4.19}$$

This shows that the Fermi level will generally be close to the middle of the band gap and will be in the middle of the band gap for pure semiconductors in equilibrium.

4.3 Impurities and Doping

In the last section, we dealt for the most part with pure or intrinsic semiconductors. Now lets suppose that the crystal is altered by introducing an impurity atom or structural defect. These alterations change the distribution of energy levels and are normally localised assuming the defects are small. If these alterations or defects occur in the band gap then the electronic properties will be altered. Introducing occupied energy levels near the conduction band will increase the Fermi energy, which will then increase the density of electrons relative to holes in equilibrium. In a similar way introducing unoccupied energy levels near the valence band will lower the Fermi energy and increase the number of holes relative to electrons. The deliberate adding of impurities close to the conduction or valence band is called doping.

4.3.1 n type doping

In n type doping, the semiconductor has been doped to increase the density of electrons relative to the holes. This can accomplished by introducing atoms with one to many valence electrons for the number of crystal bonds. These atoms are called donor atoms because they introduce an extra electron to the lattice. An example is arsenic, which has five valence electrons in silicon, which has four valence electrons. The extra electron in arsenic is much less bound then the other four involved in the strong covalent bond. As a result it is held rather loosely and can be ionised relatively easily, leaving the donor atom positively charged. The donor electrons normally have enough energy at room temperature to be fully ionised into the conduction band and since the donor sites are all filled at $T = 0$ then the Fermi energy must lie between the donor level and E_c.

The density of carriers is increased when the level of dopents is increased, N_d and if $N_d \gg n_i$, then (assuming all donors are ionised at room temperature)

$$n \approx N_d \tag{4.20}$$

and from equation4.17

$$p = \frac{n_i^2}{N_d} \tag{4.21}$$

The electron density is now increased much more relative to the hole density. The electrons are called the majority carriers and the holes are called the minority carriers. Also relative to the intrinsic case, the density of carriers is greatly increased which also increases conductivity.

4.3.2 p type doping

Similar to n type doping, p type doping is when the density of positive carriers are increased relative to negative carriers and of course this is due to doping. This can be achieved by replacing some of the atoms in the crystal by acceptor atoms, which contribute to few valence electrons to the bonds. The acceptor becomes ionised by removing a valence electron from another bond to complete the bonding between its neighbors. This releases a hole in the valence band. Once again the Fermi level will lie between the acceptor level and E_v. For a doping density $N_a \gg n_i$,

$$p \approx N_a \tag{4.22}$$

and again from equation 4.17

$$n = \frac{n_i^2}{N_a} \tag{4.23}$$

Doping is very important in photovoltaic systems because, unlike heating and illumination, it is a way of increasing the conductivity in a semiconductor at equilibrium without needing a constant input of energy.

4.4 Under Bias-Displaced from Equilibrium

Up to this point all the discussion has been when the semiconductor is in equilibrium and one feature of equilibrium is that no current flows. We know that in a photovoltaic device current flows, therefore the device cannot be in equilibrium. So what happens when sunlight displaces the device out of equilibrium?

4.4.1 Quasi thermal equilibrium and densities under bias

One of the major simplifications in semiconductor physics has been the idea of ‘quasi’ thermal equilibrium. When the semiconductor is not in equilibrium from either light energy greater then the energy gap or by electrical injection of electrons or holes from an electrical bias, the electron and hole densities are disturbed. Now if this disturbance isn’t that great or changing to quickly, the populations of electrons and holes relax to quasi thermal equilibrium. This means that the electrons in the conduction band will reach an equilibrium with a Fermi level E_{F_n} and temperature. While the holes in the valence band will reach an equilibrium with a Fermi level E_{F_p} and temperature. In this quasi equilibrium, the Fermi Dirac distribution function is approximately

$$f(E, E_{F_n}, T_n) \tag{4.24}$$

for electrons and

$$f(E, E_{F_p}, T_p) \tag{4.25}$$

for holes. This approximation is very possible because of the relaxation times within the band are much faster then those between the bands.

The densities of the holes and electrons under bias are very similar to equations 4.13 and 4.16,

$$n = N_c e^{-(E_c - E_{F_n})/kT_n} \tag{4.26}$$

$$p = N_v e^{-(E_{F_p} - E_v)/kT_p} \tag{4.27}$$

and T_n/T_p are the effective electron and hole temperatures. These temperatures can be different then the ambient T but in general it is assumed that $T_n = T_p = T$. Also, it is assumed that $E_c - E_{F_n} \gg kT$ and $E_{F_p} - E_v \gg kT$. Now when the product of np is taken, we see that the Fermi levels are split to get

$$\Delta\mu = E_{F_n} - E_{F_p} \tag{4.28}$$

$$np = n_i^2 e^{\Delta\mu/kT} \tag{4.29}$$

4.4.2 Current densities under bias-drift and diffusion

Under the influence of an applied electric field, F, a randomly moving free electron would have an acceleration $a = qF/m$ in the direction opposite from the field. However when the electron is in a crystal, the situation is different. The mass is different from the various forces and will only accelerate for so long before colliding into an impurity, another atom, or defect. The average time before collision is called the relaxation time, t_r. The average velocity increase of electrons between collisions caused by the field is called drift velocity and is given by

$$v_d = \frac{1}{2}at = \frac{1}{2}\frac{qt_r}{m_c^*}F \tag{4.30}$$

for the electrons in the conduction band. The current density flow due to the conduction band electrons is

$$J_n = qnv_d = q\mu_n nF \tag{4.31}$$

$$\mu_n = \frac{qt_r}{m_c^*} \tag{4.32}$$

and the analogous equation, by similar logic, holds for holes in the valence band.

$$J_p = q\mu_p nF \tag{4.33}$$

$$\mu_p = \frac{qt_r}{m_v^*} \tag{4.34}$$

The total current flow would then just be the sum of the two current densities. The resulting conductivity can be found to be then;

$$\sigma = \frac{J}{F} = q\mu_n n + q\mu_p p \tag{4.35}$$

Carriers in semiconductors can also flow by diffusion. It is known that excess particles will dissipate itself unless constrained, as an example think of air molecules in a balloon that dissipate after a few days. The basic cause of this is random thermal velocity of the particles. To derive the current density corresponding to diffusion, we realize that the flux of particles is proportional to the negative concentration gradient. Current is proportional to the flux of charged particles so the current density for electrons in the conduction band is just

$$J_n = qD_n\nabla n \tag{4.36}$$

and for holes in the valence band

$$J_p = -qD_p\nabla p \tag{4.37}$$

Drift and diffusion processes are fundamentally related and the constants are not independent, they are related by what is called Einstein relations;

$$D_n = \frac{kT}{q}\mu_n \tag{4.38}$$

$$D_p = \frac{kT}{q}\mu_p \tag{4.39}$$

with kt/q being equal to 26 mV at room temperature.

Chapter 5

Generation, Recombination, and Transport Equations

5.1 Introduction

This chapter lays out the basic equations that describe the ideal properties of semiconductor devices and the generation and recombination of the charge carriers. Since the main function of the photovoltaic device is the generation of photocurrent, it is important to study the physics governing electronic transitions.

5.2 Transport Equations

There are two basic principals that govern the transport equations, the number of carriers of each type must be conserved and the that the electrostatic potential obeys Poisson's equation. For a semiconductor that contains electrons and holes, the conservation of electrons requires

$$\frac{\partial n}{\partial t} = \frac{1}{q}\nabla J_n + G_n - U_n \tag{5.1}$$

and similarly for holes

$$\frac{\partial p}{\partial t} = -\frac{1}{q}\nabla J_n + G_p - U_p \tag{5.2}$$

where G and U are the volume rate of generation and recombination for carriers. These continuity equations above are relatively easy to understand and are completely general. To see this we will just considers electrons and assume the process is the very similar for holes. Lets say in a unit time, there are $V \times G_n$ electrons generated and $V \times U_n$ electrons removed. Electrons may also be introduced and removed by through current flow through the volume of interest. Now in a unit time there could be $\frac{1}{q}J_n(x+\delta x)A$ leaving the area and $\frac{1}{q}J_n(x)A$ entering the area. This leaves the net rate of $\frac{1}{q}J_n(\delta x)A$. Once can see that adding the three contributions yield equation 5.1 and 5.2. The last equation is Poisson's equation, which is;

$$\nabla^2 \phi = \frac{q}{\epsilon_s}(-\rho_{fixed} + n - p) \tag{5.3}$$

where ϕ is the electrostatic potential, ϵ_s is the dielectric permittivity of the material, and ρ_{fixed} is the local charge density.

If we can figure out how J, G and U depend on n, p and ρ, plus some other environmental parameters we have a set of coupled three differentials equations with three unknowns. These equations, in theory, can be solved since there will be three unknowns with three equations.

5.3 Principals of generation and recombination

Generation is an excited electronic state which increases the number of free carriers in the the semiconducting device and requires energy. While recombination is an electronic relaxation event that reduces the number of free carriers in the semiconducting device and releases energy. The energy can come from photons, phonons, or kinetic energy from another carrier. When there is generation, there is recombination that is equivalent to the generation.

Generation can be the promotion of an electron from the valence to conduction band, this creates an electron hole pair, from the valence to localised state in the band gap to create just a hole, or from a localised state to the conduction band to create just an electron. The most important form of generation is optical, by absorption of a photon.

Recombination is the loss of an electron or hole from the decay of an electron to a lower energetic state. This can happen from the conduction band to the valence band, from the conduction band to trap state in the band gap, or from the trap state in the band gap to the valence band. The energy released can be by an emission of a photon (radiative), as heat by phonon emission (non-radiative), or as kinetic energy to another free carrier (Auger recombination).

5.4 Fermi's golden rule

Electronic transitions can be describe through a quantum mechanical description called Fermi's golden rule and it is based on perturbation theory. The rule states that transition probability per unit time from an initial state $|i\rangle$ of energy E_i to a final empty state $|f\rangle$ of energy E_f which differs in some energy E is given by

$$\frac{2\pi}{\hbar}|\langle i|H^{'}|f\rangle|^2\delta(E_f - E_i \mp E) \tag{5.4}$$

The delta function assures conservation of energy. The minus sign comes from an excitation event and the positive sign comes from a relaxation event. The derivation of this equation is in all standard Quantum Mechanical textbooks for the motivated reader.

Let us know consider just a two level system for simplicity. The photon energy is equal to the band gap or difference between the two energies E_v and E_c. We can assume that the system is in quasi thermal equilibrium with the Fermi levels equal to E_{F_p} and E_{F_n}. There are three events that can occur and they are; photon is absorbed and electron is promoted from valence band to conduction band, the electron can relax from the conduction band back down to the valence band (spontaneous), or a photon can stimulate an excited excited electron to release a second photon of the same energy which will relax the electron to the valence band.

Absorption and stimulated emission are very closely related and can be distinguished only by the relative occupation probabilities of the two levels, any photon can cause either type of action. So the net absorption amount is

$$r_{abs} = \frac{2\pi}{\hbar}|\langle i|H_{cv}|f\rangle|^2 f(f_v - f_c) \tag{5.5}$$

where f is the probability that there is a photon, f_v is the probability that there is a electron in E_v

$$f_v = \frac{1}{e^{(E_v - E_{F_p})/kT} + 1} \tag{5.6}$$

and f_c is the probability that there is an electron in E_c.

$$f_c = \frac{1}{e^{(E_c - E_{F_n})/kT} + 1} \tag{5.7}$$

The spontaneous emission rate is just

$$r_{sp} = \frac{2\pi}{\hbar} |\langle i|H_{cv}|f\rangle|^2 f_c(1 - f_v) \tag{5.8}$$

Now, it must be noted that the matrix element is the same for both the absorption and spontaneous emission even though the initial and final states have been exchanged. With this knowledge, we know that in the steady state condition;

$$\begin{aligned} r_{abs} &= r_{sp} && (5.9) \\ f_c(1 - f_v) &= f(f_v - f_c) && (5.10) \end{aligned}$$

and after some algebra;

$$f = \frac{1}{e^{(E-\Delta\mu)/kT} - 1} \tag{5.11}$$

where $E = E_c - E_v$ and $\Delta\mu = E_{F_n} - E_{F_p}$.

5.4.1 Photogeneration

The most important generation in photovoltaic's is photogeneration, which is the generation of electrons and holes by the absorption of light in the semiconductor material. The absorption coefficient $\alpha(E)$ describes how light is attenuated in the material. Lets say that there is a beam of photons with energy E and an intensity I_0 incident normal to the material. A fraction of those photons will be attenuated by the factor $e^{-\alpha(E)dx}$. So for intensity at a distance x in the material will be;

$$I(x) = I(0)e^{-\int_0^x \alpha(x)dx} \tag{5.12}$$

To simplify the expression, assume the material is uniform to get $I(x) = I(0)E^{-\alpha x}$. It is shown that α is related to the imaginary part of the refractive index n_s. Now, if all the photons that are absorbed generate free carriers then the rate at which these are generated is simply

$$g(E, x) = b(E, x)\alpha(E, x) \tag{5.13}$$

per unit volume at a distance x below the surface and where $b(E, x)$ is just the photon flux at x. To relate the incident flux to the photogeneration rate, reflection at the surface and the attenuation constant is needed

$$g(E, x) = (1 - R(E))\alpha(E)b_s(E)e^{-\int_0^x \alpha(x)dx} \tag{5.14}$$

where $R(E)$ is just the reflectivity of the surface to incident light normal to surface. To find the total generation rate we to sum over all photon energies so

$$G(x) = \int g(E, x) dE \tag{5.15}$$

and the limits of the integral are over the energies necessary to produce carriers. So how is this attenuation constant determined? Well, it must be strongly related to the density of valence and conduction band states since it involves the promotion of an electron from the valence band to the conduction band, so we could use Fermi's golden rule. I am just going to show the results of the analysis with the estimates

$$\alpha(E) = \alpha_0 (E - E_g)^{1/2} \tag{5.16}$$

where α_0 is material dependent for direct gap semiconductors, which are when the conduction band minimum and valence band maximum occur at the same value of **k** and

$$\alpha \propto (E - E_g)^2 \tag{5.17}$$

for indirect gap semiconductors. These types of semiconductors have the minimum value of the conduction band and the maximum value of the valence band occurring at different values of **k**.

5.5 Recombination

When a semiconductor is illuminated, there are electron and hole pairs created. This creates an excess of carriers as compared to the dark. When there is no light, the electrons and holes will recombine back to their equilibrium values. This is known as the recombination process and there are many different ways this can happen, which can occur in parallel. This section will briefly describe some of these processes.

5.5.1 Radiative Recombination

Radiative recombination is the the reverse of the absorption process and is unavoidable. An electron that occupies an excited state will make the transition to the lower energy state by emission of a photon in thermal equilibrium. Radiative recombination occurs more frequently in direct band gaps then in indirect band gap because of the two step process involving a phonon. This derivation, as one could imagine, involves the absorption coefficient however we are going to use simple arguments here.

The total radiative recombination rate is proportional to the product of the concentrations of the electrons and holes;

$$R_{rad} = B_{rad} np \tag{5.18}$$

where B_{rad} is a constant (dependent on the absorption constant) of the material. Explicitly it is;

$$B_{rad} = \frac{1}{n_i^2} \frac{2\pi}{h^3 c^2} \int_0^\infty n_s^2 \alpha(E) e^{-E/kT)} E^2 dE \tag{5.19}$$

Now when the semiconductor is in thermal equilibrium $n_i^2 = np$, the recombination rate is balanced by the equal and opposite generation rate. The net recombination rate, U_{rad}, is given by the total recombination rate minus the equilibrium rate.

$$U_{rad} = B_{rad}(np - n_i^2) \tag{5.20}$$

Associated with the recombination rates are the carrier lifetimes, $\tau_{n,rad}$ and $\tau_{p,rad}$ that are just

$$\tau_{n,rad} = \frac{n - n_0}{U_{rad}} = \frac{\Delta n}{U_{rad}} \tag{5.21}$$

$$\tau_{p,rad} = \frac{p - p_0}{U_{rad}} = \frac{\Delta p}{U_{rad}} \tag{5.22}$$

where Δn and Δp are just the the change from the carrier concentration to equilibrium concentration. Radiative recombination is relatively unimportant in real devices but for perfect material it limits efficiency.

5.5.2 Auger Recombination

Auger recombination is when the electron recombining with the hole give the excess energy to another electron. The second electron is excited but relaxes back down to its original energy by emitting a phonon. This process involves either a electron and two holes or two electrons and one hole. Similarly, we can assume that the recombination rate is proportional to the densities of all three carriers and the net rate is

$$U_{Aug} = A_p(n^2 p - n_0^2 p_0) \tag{5.23}$$

for two electrons and

$$U_{Aug} = A_n(np^2 - n_0p_0^2) \tag{5.24}$$

for two holes. When the densities are high, Auger recombination is very important. Once again the carrier lifetimes are defined and given as

$$\tau_{n,Aug} = \frac{1}{A_nN_a^2} \tag{5.25}$$

$$\tau_{p,Aug} = \frac{1}{A_pN_d^2} \tag{5.26}$$

5.5.3 Shockley Read Hall Recombination

This kind of recombination is the most important for real semiconductors, as they involve defects or trap states. The defect levels create a two step recombination process where the electrons can relax from the conduction band to the defect level, then down to the valence band and finally recombining with the hole. For simplicity, the recombination for a single defect level is shown below without the details,

$$U_{SRH} = \frac{np - n_i^2}{\tau_{n,SRH}(p+p_t) + \tau_{p,SHR}(n+n_t)} \tag{5.27}$$

where n_t and p_t arise from the analysis which depend on the trapping energy level E_t.

$$n_t = N_ce^{(E_t-E_c)/kT} \tag{5.28}$$

$$p_t = N_ve^{(E_v-E_t)/kT} \tag{5.29}$$

Also, the carrier lifetimes are defined as

$$\begin{aligned} \tau_{n,SRH} &= \frac{1}{B_nN_t} && (5.30)\\ B_n &= v_n\sigma_n \\ \tau_{p,SRH} &= \frac{1}{B_pN_t} && (5.31)\\ B_p &= v_p\sigma_p \end{aligned}$$

$v_{n/p}$ are the mean thermal velocities and $\sigma_{n/p}$ are the capture cross sections of the trap for electrons and holes respectively. For p doped semiconductors equation 5.27 can be simplified as $\tau_{n,SRH}N_a \gg \tau_pn_t$ and $N_a \gg p_t$;

$$U_{SRH} \approx \frac{\Delta n}{\tau_{n,SRH}} \tag{5.32}$$

and for n doped semiconductors;

$$U_{SRH} \approx \frac{\Delta p}{\tau_{p,SRH}} \tag{5.33}$$

5.5.4 Surface Recombination

Surfaces have many more defects and allow for many states within the forbidden gap. Therefore we should expect the recombination to be similar to that of the SRH equation above. The net recombination rate per unit area for a single surface state is

$$U_s = \frac{n_s p_s - n_i^2}{\frac{1}{S_n}(p_s + p_t) + \frac{1}{S_p}(n_s + n_t)} \tag{5.34}$$

where n_s and p_s are the electron and hole densities at the surface. S_p and S_n are the surface recombination velocities directed toward the surface.

Chapter 6

p-n Junction

6.1 Introduction

The previous two chapters discussed the photogeneration and charge transport in the semiconductor. The last important concept of a photovoltaic device is charge separation, which requires some sort of driving force. This driving force can come from many different mechanisms which will be discussed in this chapter.

When a semiconductor that is n type doped is brought together in contact with a semiconductor that is p type doped, a p-n junction is formed. This junction will act as a barrier to carrier charge flow and allow electrons or holes a low resistance path to the n or p contact. The problem is solving the coupled differential equations which are extremely complex but with some assumptions, analytical solutions for $J(V)$ are found.

6.2 Electrostatics of the p-n junction

When the two doped semiconductors are brought together to form a junction, it can be expected that the electrons regions of high concentration (n type) will flow to the region of low concentration (p type) and vice versa for holes. However as the electrons flow from the n type region, the net charge would be positive. As the holes from the p type region, the net charge would be negative. This charge imbalance sets up an electric field that will oppose the diffusion. The equilibrium will occur when the diffusion of majority carriers are balanced by the drift of minority carriers back across the junction, the Fermi levels are equal now. Far enough away from the junction, conditions will look like as if each semiconductor is isolated.

Therefore, there must be some transition region near the junction where there is a potential change, V_{bi} and this can be found by considering the difference in work functions of the two materials. Where the work function is defined as the potential required to remove the least tightly bound electron, $\Phi_w = (E_{vac} - E_F)$.

$$\begin{aligned} qV_{bi} &= E_g - E_{pregion} - E_{nregion} \qquad (6.1) \\ E_{pregion} &= E_F - E_v = kTln\left(\frac{N_v}{N_a}\right) \\ E_{nregion} &= E_c - E_F = kTln\left(\frac{N_c}{N_d}\right) \end{aligned}$$

and now simplify using equation 4.17 to find.

$$V_{bi} = \frac{kT}{q} ln\left(\frac{N_a N_d}{n_i^2}\right) \qquad (6.2)$$

This equation relates the doping levels to V_{bi}. If there is an applied bias, V, this will change the potential difference across the transition region, $V_j = V_{bi} - V$. A positive applied bias will inject carriers into the junction region, while a negative applied bias will further deplete the junction region of carriers. Light illumination causes holes to be built up in the p side and electrons on the n side which shifts the Fermi level in the same way as a positive applied bias.

Using the first approximation, known as the depletion approximation ($\rho_{fixed} = 0$ in the transition region), we can solve Poisson's equation to find the depletion width. Setting up the equations we have;

$$\frac{d^2\phi}{dx^2} = \frac{q}{\epsilon_s} N_a \quad \text{for} \quad x < 0 \qquad (6.3)$$

$$\frac{d^2\phi}{dx^2} = -\frac{q}{\epsilon_s} N_d \quad \text{for} \quad x > 0 \qquad (6.4)$$

The boundary conditions being that ϕ can only vary in the depletion region from 0 at $x = -w_p$ to V_{bi} at $x = w_n$ and that the field must vanish at the edge of the depleted layers, we have after integrating Poisson's equations

$$-\frac{d\phi}{dx} = -\frac{qN_a}{\epsilon_s}(x + w_p) \quad \text{for} \quad -w_n < x < 0 \qquad (6.5)$$

$$-\frac{d\phi}{dx} = \frac{qN_d}{\epsilon_s}(x - w_n) \quad \text{for} \quad 0 < x < w_p \qquad (6.6)$$

and finally after one more integration using the boundary conditions on ϕ yield

$$\phi = \frac{qN_a}{2\epsilon_s}(x+w_p)^2 \quad \text{for} \quad -w_n < x < 0 \tag{6.7}$$

$$\phi = -\frac{qN_d}{2\epsilon_s}(x-w_n)^2 + V_{bi} \quad \text{for} \quad 0 < x < w_p \tag{6.8}$$

and finally requiring that ϕ be continuous at $x = 0$ we get the depleted widths

$$w_p = \frac{1}{N_a}\left(\frac{2\epsilon_s V_{bi}}{q(\frac{1}{N_a}+\frac{1}{N_d})}\right)^{1/2} \tag{6.9}$$

$$w_n = \frac{1}{N_d}\left(\frac{2\epsilon_s V_{bi}}{q(\frac{1}{N_a}+\frac{1}{N_d})}\right)^{1/2} \tag{6.10}$$

$$w_{dep} = w_p + w_n = \left(\frac{2\epsilon_s V_{bi}}{q}\left(\frac{1}{N_a}+\frac{1}{N_d}\right)\right)^{1/2} \tag{6.11}$$

This equation shows that as the doping of either p or n is decreased, the depletion width increases.

6.3 Current and Carrier Densities

6.3.1 Current and carrier densities outside of the depleted region

In order to find the carrier densities, equations 5.1 and5.2 need to be solved. In the neutral regions, the electric field is zero and the doping levels are constant. If recombination is linear (second assumption) then we have in the p region with some manipulation;

$$\frac{d^2n}{dx^2} - \frac{(n-n_0)}{L_n^2} + \frac{g(E,x)}{D_n} = 0 \quad \text{for} \quad x < -w_p \tag{6.12}$$

where $g(E,x)$ is just equation 5.14 for uniform material. L_n is the diffusion length, defined $\sqrt{\tau_n D_n}$. At the boundary of the depletion region,

$$n - n_0 = \frac{n_i^2}{N_a}(e^{qV/kT}-1) \quad \text{for} \quad x = -w_p \tag{6.13}$$

$n_0 = n_i^2/N_a$ is the equilibrium electron density in the p region. This comes from the boundary condition $E_{F_n} - E_{F_p} = qV_j$ throughout the depleted region. Now the second boundary condition, just going to state, comes from surface recombination at the outer most surface

$$D_n \frac{dn}{dx} = S_n(n - n_0) \quad \text{at the surface} \quad x = -x_p \tag{6.14}$$

and remembering that since the electron current is completely diffuse (no electric field).

$$j_n(E, x) = qD_n \frac{dn}{dx} \tag{6.15}$$

Also, for a thick p region (compared to L_n) the boundary condition $n(-x_p) = n_0$ will be sufficient. Using similar logic for the n region

$$\frac{d^2p}{dx^2} - \frac{(p - p_0)}{L_p^2} + \frac{g(E, x)}{D_p} = 0 \quad \text{for} \quad x > w_n \tag{6.16}$$

and the boundary conditions being;

$$p - p_0 = \frac{n_i^2}{N_d}(e^{qV/kT} - 1) \quad \text{for} \quad x = w_n \tag{6.17}$$

$$-D_p \frac{dp}{dx} = S_p(p - p_0) \quad \text{for} \quad x = w_n \tag{6.18}$$

again, $p_0 = n_i^2/N_d$. The hole current density is just

$$j_p(E, x) = -qD_p \frac{dp}{dx} \tag{6.19}$$

6.3.2 Current and carrier densities in the depleted region

The depleted region is assumed to have no free carriers and since E_{F_n} and E_{F_p} are constant across this region so;

$$\begin{aligned} E_{F_n}(x) &= E_{F_n}(w_n) \\ E_{F_p}(x) &= E_{F_p}(-w_p) \\ qV &= E_{F_n}(x) - E_{F_p}(x) \quad \text{for} \quad -w_p < x < w_n \end{aligned} \tag{6.20}$$

Now, n and p are just

$$n = n_i e^{(E_{F_n} - E_i)/kT} \tag{6.21}$$

$$p = p_i e^{(E_i - E_{F_p})/kT} \tag{6.22}$$

where E_i is called the intrinsic potential energy and is found from $E_i = -q\phi$ (ϕ is just a solution to Poisson's equation). Equations 6.21 and 6.22 are just different forms of equations 4.26 and 4.27. Using equations 5.1 or 5.2, we can calculate the net electron current generated between $-w_p$ and w_n and the net hole current generated between w_n and $-w_p$.

$$J_{dep} = q\int_{-w_p}^{w_n}(U-G)dx \tag{6.23}$$

U is found from n and p given from the recombination rate and G is known from the incident spectrum.

6.3.3 Total current density

The net current is given in terms of the sum of the contributions from J_n and J_p at any point in the device. It must be constant during the steady-state. Evaluating J at $-w_p$ yields;

$$\begin{aligned} J &= -J_n(-w_p) - J_p(-w_p) \\ J &= -J_n(-w_p) - J_p(w_n) - J_{dep} \\ J &= -\int j_n(E,-w_p)dE - \int j_p(E,w_n)dE - \int j_{dep}(E)dE \end{aligned} \tag{6.24}$$

using the result from the continuity equations;

$$J_p(-w_p) = J_p(w_n) + \int_{-w_p}^{w_n}(U-G)dx \tag{6.25}$$

$j_n(E,-w_p)$ and $j_p(E,w_n)$ are found by evaluating equations 6.15 and 6.19 at edges of the depleted region using the solutions $n(x)$ and $p(x)$.

6.4 p-n Junction under illumination

The analytic solutions for $n(x)$ and $p(x)$ in equations 6.12 and 6.16 are extremely complex and solutions for $j_n(E,-w_p)$ and $j_p(E,w_n)$ are even more complicated. Therefore, they are omitted here and only the approximate forms are shown for the junction under illumination.

6.4.1 Short circuit

As noted before, when the junction is illuminated electron hole pairs are created in all the regions. Since n and p are enhanced above their equilibrium value, the respective Fermi levels are split. The electric field at the junction acts to separate the pairs by driving the minority carriers across the junction. The short circuit current, J_{sc}, is the first property that is going to be discussed ($V = 0$). The Fermi levels in the depleted region are equal to each other in this case from equation 6.20 and there is no net recombination. For the minority carrier currents from the neutral regions;

$$j_n(E, -w_p) = \left[\tfrac{qb_s(1-R)\alpha L_n}{(\alpha^2 L_n^2 - 1)}\right] \times \left(\frac{(\frac{S_n L_n}{D_n} + \alpha L_n) - e^{-\alpha(x_p - w_p)}(\frac{S_n L_n}{D_n} \cosh \frac{(x_p - w_p)}{L_n} + \sinh \frac{(x_p - w_p)}{L_n})}{\frac{S_n L_n}{D_n} \sinh \frac{(x_p - w_p)}{L_n} + \cosh \frac{(x_p - w_p)}{L_n}} - \alpha L_n e^{-\alpha(x_p - w_p)} \right) \tag{6.26}$$

and $j_p(E, w_n)$

$$= \left[\tfrac{qb_s(1-R)\alpha L_p}{(\alpha^2 L_p^2 - 1)}\right] e^{-\alpha(x_p + w_n)} \left(\alpha L_p - \frac{\frac{S_p L_p}{D_p}(\cosh \frac{(x_n - w_n)}{L_p} - e^{-\alpha(x_n - w_n)}) + \sinh \frac{(x_n - w_n)}{L_p} + \alpha L_p e^{-\alpha(x_n - w_n)}}{\frac{S_p L_p}{D_p} \sinh \frac{(x_n - w_n)}{L_p} + \cosh \frac{(x_n - w_n)}{L_p}} \right) \tag{6.27}$$

and finally,

$$j_{dep}(E) = qb_s(1 - R)e^{-\alpha(x_p - wp)}(1 - e^{-\alpha(w_p + w_n)}) \tag{6.28}$$

The total short circuit current density found from equation 6.24. The quantum efficiency of the cell defined in chapter 2 can be found from the short circuit photocurrent by

$$QE(E) = \frac{-j_n(E, -w_p) - j_p(E, w_n) - j_{dep}(E)}{qb_s}. \tag{6.29}$$

This is easy to obtain since all the terms in the photocurrent are proportional to b_s, notice that quantum efficiency doesn't depend on the the incident spectrum.

6.4.2 Some Approximations to Photocurrent and QE

In the last section, we saw the form for the short circuit photocurrent and realized how complicated it is. Some approximations can be made to the photocurrent if some limiting cases are considered. First, lets take a look at when the both the neutral layers are much thicker then the diffusion length. The electron and hole currents are then

$$j_n(E,-w_p) \approx qb_s(1-R)e^{-\alpha(x_p-w_p)}\left(\frac{\alpha L_n}{1-\alpha L_n}\right) \tag{6.30}$$

$$j_p(E,w_n) \approx qb_s(1-R)e^{-\alpha(x_p+w_n)}\left(\frac{\alpha L_p}{1+\alpha L_p}\right) \tag{6.31}$$

and in the other limit, as L_n and L_p are much longer then the p and n regions the forms are

$$j_n(E,-w_p) \approx qb_s(1-R)\left(1+\frac{S_n}{\alpha D_n}\right)(1-e^{-\alpha(x_p-w_p)} \tag{6.32}$$

$$j_p(E,w_n) \approx qb_s(1-R)e^{-\alpha(x_p+w_n)}\left(1+\frac{S_p}{\alpha D_p}\right)(1-e^{-\alpha(x_n-w_n)} \tag{6.33}$$

If no carriers are lost through the surface ($S_n = 0$ and $S_p = 0$), then the photocurrents are just q times the flux of the absorbed photons.

The quantum efficiency measures the cell design and material. The short wavelength activity is normally provided by the p region, since the high energy photons are absorbed at the front of the cell. Carriers generated at the front of the cell are suspect to surface recombination, so high energy photons are sensitive to this. Surface recombination may be reduced by introducing a window layer at the surface. Long wavelength's are affected by the back of the surface. The quantum efficiency for these wavelength's is affected by the thickness and surface quality. The in-between wavelength's generate carriers in the depleted region. The overall quantum efficiency is affected by the efficiency of light absorption, which may be increased by light trapping techniques, reducing reflection losses, and increasing the width of the cell.

6.4.3 Example of Quantum Efficiency

Suppose that a solar cell has emitter thickness of x_n (top layer) and a base thickness of x_p (bottom layer). The front surface reflectivity is R and absorption coefficient of α for photons of energy E, then the photon flux density would be

$$= b_0(E)(1-R)e^{-\alpha x_n} \tag{6.34}$$

if incident flux is b_0. Now the absorbed photon flux density in the base would be

$$= b_0(E)(1-R)e^{-\alpha x_n}(1-e^{-\alpha x_p}) \tag{6.35}$$

If we assume that for every absorbed photon in the base results in one electron delivered to the external circuit, the photocurrent would just be

$$J = qb_0(E)(1-R)e^{-\alpha x_n}(1-e^{-\alpha x_p}) \tag{6.36}$$

Finally the quantum efficiency would just be

$$\begin{aligned} QE(E) &= \frac{qb_0(E)(1-R)e^{-\alpha x_n}(1-e^{-\alpha x_p})}{qb_0(E)} && (6.37)\\ &= (1-R)e^{-\alpha x_n}(1-e^{-\alpha x_p}) && (6.38) \end{aligned}$$

6.4.4 p-n junction as a photovoltaic cell

When a load of resistance is connected between the contacts when illuminated, the cell experiences both electrical and optical bias. The bias splits the Fermi levels throughout the device. The Fermi levels slope toward the band edge at the edges of the depleted region. This indicates that the net current is negative.

Since the solutions for bias and light induced currents are independent in the depletion approximation, the current is given the by sum of the short-circuit photocurrent and the dark current at bias. Dark current can be dominated by diffusion current and if this is the case then;

$$\begin{aligned} J_{dark} &= J_{diff,0}(e^{qV/kT}-1) && (6.39)\\ J_{diff,0} &= qn_i^2\left(\frac{D_n}{N_aL_n}+\frac{D_p}{N_dL_d}\right) \end{aligned}$$

and we get for the current,J

$$J(V) = J_{sc} - J_{diff,0}(e^{qV/kT}-1) \tag{6.40}$$

This form is identical to the ideal diode equation that was first explored as equation 2.4 and is most commonly used form for the current voltage characteristic of a solar cell. However, sometimes the current equation can be used as a non-ideal diode equation and if that is the case then,

$$J(V) = J_{sc} - J_{m,0}(e^{qV/mkT} - 1) \tag{6.41}$$

where $J_{m,0}$ is the saturation current in the dark. This expression is used when the recombination currents are dominant in the depleted space and $m = 2$ and $J_{m,0}$ is

$$J_{m,0} = \frac{qn_i(w_n + w_p)}{\sqrt{\tau_n \tau_p}} \tag{6.42}$$

Using the above equation, the open circuit voltage can be found when no current is drawn and is just;

$$V_{oc} = \frac{mkT}{q} ln \left(\frac{J_{sc}}{J_{m,0}} + 1 \right) \tag{6.43}$$

We can now calculate the $J(V)$ for any $p - n$ device structure when the quantum efficiency spectrum is found, along with the dark current. Then the solar cell performance characteristics can be extracted using the techniques described in chapter 2.

Chapter 7

Increasing Efficiency

The basic physics of photovoltaic systems have been introduced in the previous chapters with the following assumptions;

- One electron-hole pair in generated by each absorbed photon
- Electrons and holes relax to form populations in thermal equilibrium with the lattice
- All the light is absorbed in a junction of single band gap

Due to these constraints the majority of the suns power is lost due to the large volume of infra-red light that has insignificant energy to excite an electron to the conduction band and thermal dissipation of kinetic energy of carriers which have $E \gg E_g$. In this chapter, we are concerned if the work done per photon (efficiency) could be theoretically increased. Of course, the answer is yes by relaxing some of the assumptions listed above. Some potential solutions are

- Increase the number of band gaps to allow for different photon energies to be utilized
- Reduce the kinetic energy of carriers which have $E \gg E_g$
- Increase the number of carriers per photon.

7.1 Stacked cells

As mentioned previously, one of the major energy losses in the single junction cell is the thermalisation of excited carriers with those with energy well above the energy gap. One way to reduce this is to subdivide the solar spectrum into different energy ranges so that each range could be matched up the its proper bandgap. This is called spectral splitting and this could be achieved through spectral sensitive mirrors. However, in practice it was realized very quickly that spectral splitting could be automatically achieved by stacking cells on top of one another with the largest bandgap cell as the top cell and decreasing the bandgap along the way down.

When the cells are stacked, there is an opportunity for the interaction between the cells. Think of a cell that is in between two other cells, it receives light energy that has all the high energy photons removed and also emits light from both its surfaces while receiving light emitted by the cells next to it. There is a recycling of photons going on in this setup and of course this introduces additional terms in the performance of each cell.

7.1.1 Two Terminals

Stacked cells are normally operated as two terminal devices, where the cells are connected in series so that a single current passes and the voltages can be added. However, this constrains the performance because the currents from each cell have to be matched. This constrains the performance and maximum output is slightly diminished. As the number of cells increase, larger fluctuations in the current output of the cells will become likely.

7.1.2 Infinite Number of Cells

When an infinite number of cells are considered, it puts the upper most limit on the efficiency of the stacked cell approach. Therefore, this theoretical limit will give some insight on the constraints of this approach.

For the infinite number of cells, each cell converts photons over the infinitesimal energy range dE. The current voltage relationship is

$$J = \frac{2q\pi}{h^3c^2}\left(\frac{f_sE^2}{e^{E/kT_s}-1} + \frac{(1-f_s)E^2}{e^{E/kT_c}-1} - \frac{E^2}{e^{(E-qV)/kT_c}-1}\right)dE \tag{7.1}$$

where $f_s = 1/4.6 \times 10^4$ is the reduced factor from the sun angle introduced in chapter 3 for diffuse cells. The optimum operating voltage can be found by the procedure before, multiply by V and then differentiate and set to 0. This turns out to be;

$$\frac{f_s}{e^{E/kT_s}-1} + \frac{1-(f_s)}{e^{E/kT_c}-1} - \frac{(1+qV_m/kT_c)(e^{(E-qV_m)/kT_c}-1)}{(e^{(E-qV_m)/kT_c}-1)^2} = 0 \tag{7.2}$$

The optimum efficiency for the infinite stack cell approach is given by;

$$\eta = \frac{15q}{f_s\pi^4k^4T_s^4}\int_0^\infty\left(\frac{f_sV_mE^2}{e^{E/kT_s}-1}+\frac{(1-f_s)V_mE^2}{e^{E/kT_c}-1}-\frac{V_mE^2}{e^{(E-qV_m)/kT_c}-1}\right)dE \tag{7.3}$$

For each energy, the voltage of the infinite stack approach can be adjusted to find the optimum V_m, and it turns out that this makes the calculated efficiency limits of 86.6% for direct cells and 68.2% for diffuse cells.

7.1.3 Example-Finding V_m

Lets assume an infinite stack of cells capable of converting diffuse radiation and assuming $T_s = 6000$K and $T_c = 300$K. Cells have the bandgap 0.25eV, 0.50eV, and 2.0eV. Using equation 7.2 we can find V_m. The easiest way to do this is to write a small program to scan through 0 and E_g/q (set $E = E_g$) and find the V_m value closest to 0. This was done and for the bandgap 0.25eV; $V_m = 6.0$mV, for 0.50eV; $V_m = 158$mV, and for 2.0eV; $V_m = 1.55$V.

7.2 Hot Carrier Cells

Another major loss in the cell comes from the thermalisation process of excited carriers. If this process could be avoided, then the efficiency would increase. In order to avoid this process, the carriers could still thermalise by collisions with one another to stabilize in a distribution described by a temperature much higher then the lattice temperature. Excess energy is stored in this distribution.

7.2.1 Cooling of Carriers

First, consider we shall consider what happens after an electron is promoted through absorption into the conduction band. Originally, the semiconductor is in thermal equilibrium and the electrons and holes are described by the Boltzmann distribution in the conduction and valence band. Right after illumination, there are additional photogenerated carriers which are superimposed upon the equilibrium condition. The peak in the valence band will generally lie closer to the band edge (higher effective mass) then the peak in the conduction band. Therefore, most of the energy is absorbed in the conduction band.

Right after illumination, the carriers begin to return to equilibrium. Initially, carrier-carrier collisions often occur and act to distribute the energy more uniformly, evolve toward the Boltzmann distribution but at a much higher temperature. This normally happens in < 1 picosecond (ps). During this stage, no energy is lost, it is just shared amongst the photoexcited and original carriers. The effective temperature depends on the total energy shared and could the effective temperature could be different between the electron and holes.

Next, the carriers start to lose energy through phonon emission. High energy optical phonon emission dominate during the initial part of this stage but then lower energy acoustic phonons dominate during the later part. The effective temperature decrease along with the energy and this process normally happens around 1nanosecond (ns) after illumination has ceased.

Finally, the carriers cool down to the lattice temperature ($1\mu s$) and then start to recombine with holes to reduce the number of carriers. This will happen until thermal equilibrium takes place again.

A good conventional solar cell operates with the carrier collection times of the same order as the recombination process. The cell should collect most of the carriers *after* they thermalise but *before* they recombine. A hot carrier cell works on much shorter time scales, as it has to collect the carriers before they start to cool (*before thermalisation*).

There are two important points when dealing with hot carriers. First since carriers have a finite velocity, there will be a finite distance that they travel. This gives an indication of possible collection distances (hot carriers have a thermalisation distance of $10nm$). Second, is the how the device is contacted since carriers within the contacts have the lattice temperature. If hot carriers interact with the contact carriers then they will cool. The interaction can be minimized by withdrawing the carriers across only a small range of energies, rather then across the entire conduction or valence band. This can be done by use of a wide bandgap semiconductor with narrow conduction and valence bands.

7.2.2 Analysis

Assuming that the carriers in the conduction and valence bands come to the same temperature, T_H, and the distributions could be described by quasi-Fermi energies μ_c and μ_v, the difference is

$$\Delta\mu_H = \mu_c - \mu_v \tag{7.4}$$

and to minimize interaction with the external environment, assume the carriers were removed from one specific energy in the conduction band and returned to one specific energy in the valence band. They are separated by the energy, $E_{use} = E_{c1} - Ev1$ and the extracted current can be deduced by a particle balance argument;

$$J = q[f_s\dot{N}(E_g,\infty,T_s,0) + (f_c - f_s)\dot{N}(E_g,\infty,T_a,0) - f_c\dot{N}(E_g,\infty,T_H,\Delta\mu_H)] \tag{7.5}$$

where $\dot{N}$ is the particle flux and has the form of equations 3.14 and 3.20, f_c is a geometrical factor just like f_s. Since there is no energy loss in the hot carrier formulation the energy balance can also be applied,

$$E_{use}J_{use} = f_s\dot{E}(E_g,\infty,T_s,0) + (f_c - f_s)\dot{E}(E_g,\infty,T_a,0) - f_c\dot{E}(E_g,\infty,T_H,\Delta\mu_H) \tag{7.6}$$

where $\dot{E} = E\dot{N}$ is just the energy flux. The power output is the current times the potential difference between the contacts. This doesn't equal $\Delta\mu_H/q$ because the contacts are at ambient temperature. The corresponding electrochemical potential difference in the ambient needs to be found. Equating the distributions at E_{c1} and E_{v1} gives

$$\begin{align}
\frac{E_{c1} - \mu_{cH}}{T_H} &= \frac{E_{c1} - \mu_{ca}}{T_a} \tag{7.7}\\
\frac{E_{v1} - \mu_{vH}}{T_H} &= \frac{E_{v1} - \mu_{va}}{T_a} \tag{7.8}
\end{align}$$

and we can manipulate these two equations to find

$$\Delta\mu_a = \frac{\Delta\mu_H T_a}{T_H} + \Delta_{use}(1 - \frac{T_a}{T_H}) \tag{7.9}$$

The power output then becomes;

$$\begin{align}
P_{use} &= \frac{\Delta\mu_a}{q} \times J_{use} \tag{7.10}\\
&= \frac{J_{use}\Delta\mu_H T_a}{T_H} + \Delta E_{use}\left(\frac{J_{use}}{q}\right)\left(1 - \frac{T_a}{T_H}\right) \tag{7.11}
\end{align}$$

One of the interesting features of the hot carrier cell is that there is no need for an energy gap. The reason for this is that the excited carriers are collected before they lose any energy, therefore even before the thermalisation.

7.3 Multiple Electron-Hole pairs

The idea that one photon can create multiple electron-hole pairs is a basic idea. If a high energy photon creates an electron-hole pair and the excess energy is given up by a collision with a lattice atom, then it is possible to create another electron-hole pair. This happens when the photon has twice the energy of the band gap energy. If the photon has energy three times the band gap, then you guessed it, three pairs are created.

Initially, it was thought that this would obviously improve spectral sensitivity but without a cost. However, if a photon can create multiple-hole pairs then multiple-hole pairs could create a single photon. This photon would have a different chemical potential from a photon generated by a single electron-hole recombination. More explicitly, if m electrons recombine with m holes to produce a single photon, the equilibrium free energy shows

$$m\mu_e dN_e + m\mu_h dN_h + \mu_{ph} dN_{ph} = 0 \tag{7.12}$$

Therefore, $\mu_{ph} = \mu_{eh}$. Analysis shows that single electron-hole processes are proportional to the number of these pairs and therefore to $e^{qV/kT}$. Processes involved in two of these pairs will increase as the square of their concentration, $e^{2qV/kT}$. So processes involved in m pairs will increase like $e^{mqV/kT}$. For simplicity, the power density output and efficiency are;

$$P = \frac{2\pi}{h^3c^2}\int_{E_g}^{\infty}(\frac{f_s\mu(E)}{e^{E/kT_s}-1} + \frac{(f_c-f_s)\mu(E)}{e^{E/kT_a}-1} \tag{7.13}$$

$$-\frac{f_c\mu(E)}{e^{(E-\mu(E))/kT_c}-1})E^2dE$$

where $\mu(E) = mqV$. The efficiency can be found analytically when $E_g = 0$ and the function $\mu(E) = aE/Eg$. In this case the efficiency is found to be

$$\eta = [1 - \frac{T_c}{T_s}^4 + \frac{f_c}{f_s}[(\frac{T_c}{T_s})^4 - (\frac{T_I}{T_s})^4]](1 - \frac{T_c}{T_I}) \tag{7.14}$$

and when $f_s = f_c$, this gives a peak value of 85.4%.

Part II

Feasability of Solar Energy

Chapter 8

Introduction

The second part deals with the feasability of employing solar energy systems as the majority electricity generator and why it is necessary that electricity must be generated in this manner. Energy today is a topic that is discussed at the global level by politicians, scientists, activists, environmentalists, etc. because the current world energy systems (primarly using non-renewables) will not sustain the population and continue to affect the planet adversely. Therefore, new efficient ways to generate energy will need to be put in to place in order to sustain and improve life standards.

Before the discussion of renewables begins, lets briefly review some of the problems with the current energy situation.

8.1 Problems of Fossil fuels

8.1.1 Adverse Environmental Impact

As mentioned in the the introduction to this paper, combustion of fossil fuels result in some harmful emissions like VOC's, SO_2, NO_x, CO_2, particulates etc. These pollutants contribute to harmful health effects that have been well documented, which is why there are air pollution laws and control technologies employed throughout the different nations of the world. Of course, each nation has their own pollution regulations with some being more strict then others. In the United States and under the Clean Air Act, EPA sets limits on how much of a pollutant is allowed in the air anywhere in the United States. Also, there are oil spills and other environmental problems that can be directly and indirectly related to the combustion of of fossil fuels.

8.1.2 Fossil Fuel Supply Problems

Fossil fuels will run out, there are many different opinions on when, but it is a fact that they will not be around forever. Therefore, human ingenuity will be needed to replace the current sources of energy. Obviously, the replacement(s) will have to be renewable and preferably clean/safe.

8.1.3 The Distribution of Fossil Fuels

Fossil fuels are not evenly distributed throughout the world, the top consumers and the top producers are normally not the same. For example, in 2006 the top oil producer was Saudi Arabia with 10, 719 thousand barrels per day and the top oil consumer was the United States with 20, 588 thousand barrels per day. This results in tension between nations who need oil and nations who produce it, big trade deficits, development restrain for poor countries, and of course political turmoil.

8.1.4 Price Volatility

Oil and natural gas prices, which make a big chunk of the fossil fuels, are extremely volatile. This makes it very hard to predict and cause end-user consumers economic hardship. For example, the price of crude oil in January 1999 was $9.76 per barrel and in January 2000 the price rose to $23.17 per barrel!

8.2 Renewable Positives

Renewables, which include but are not limited to hydropower, solar, biomass, wind, nuclear, and geothermal, are forms of energy that are essentially inexhaustable. This would be the next logical step in the evolution of energy production if they could be harnessed. Lets take a look at some of the positives.

8.2.1 Very Low Environmental Impact

The damage to the environment caused by the non-renewables is generally avoided by the renewables. Hydro, wind, and solar are emission free and one can argue that they are self-sustainable (very low maintenance required). Biomass, which are plants that are grown specifically for burning, don't put any additional carbon emissions in the atmosphere when viewed as a closed system. These sources of energy generally do not involve the depletion of the earth's natural resources that one day might be required for other uses besides energy.

8.2.2 More Universal Distribution

Unlike the fossil fuels that are unevenly distributed throughout the planet, renewables can be utilized by most and if not all nations. Of course there are some nations that will make better use of some rather then others. For example places on the earth where the sun is prominent, will use solar energy as its primary renewable.

8.2.3 Essentially Inexhaustable

The most important reason why renewables are much more positive then their counter part is the most straightforward one, they can be replenished! Humans will not have to worry about where the energy is going to come from anymore, if it is here today then it will be here tomorrow. This is the definition of renewable energy sources and why they are so important to our future.

Chapter 9

Renewable Options

9.1 Introduction

There is much speculation on when the fossil fuel supply will run out but whenever that time frame may be we know that the human race will outlast it. The most conservative estimates being the mid-twenty first century, which we are dangerously approaching. Therefore, if human's are to sustain at least the life standard of today then there are going to be some changes in energy generation. As mentioned before, this will come in the form of renewables. When considering these sources there are a few different options. These options are evaluated by the renewables energy flux and power density. Energy flux is very important because it represents the uppermost limit on the amount of energy available to the system. So renewables with high energy fluxes or comparable to that of fossil fuels will be looked upon with great interest.

The transition from fossil fuels to nonfossil energies should be one that does not disrupt the worlds everyday energy use (smooth transition) and should make the benefits of higher energy use (United States) available to those countries who currently don't have access to it. Actually, fossil fuels do not permit everybody on the planet to enjoy the benefits of higher energy, there simply isn't enough to go around. There are the have's and the have not's. The renewable option or options should bridge the gap between the two.

Are there renewable options that will satisfy the above criteria? The answer, of course, is yes and it comes in the form of solar radiation. This energy flux should be utilized either directly (photovoltaic's) or after its conversion to flowing water, wind, waves, or biomass. Lets take a look at some of the more popular renewable options to see which one is most promising.

9.2 Wind

Capturing wind for useful work in nothing new and has been used throughout history in the forms of windmills. Better designs and higher conversion efficienies have made wind power a major source of energy generation in Europe and the United States. In 2006 over 2,400 megawatts (MW) were installed and it is estimated that over 3000 MW will be installed in 2007. About 31 billion kilowatt-hours (kWh) will be generated by wind in the U.S., which is enough electricity to power around 3 million homes[1]. This tells us that wind is getting alot of attention and is getting cost competitive.

9.2.1 Basics of Wind Power

Winds are created by uneven heating of the atmosphere by the sun, irregularities of the Earth's surface, and the rotation of the Earth. As a result, winds are strongly influenced and modified by local terrain, bodies of water, weather patterns, vegetative cover, and other factors. The simplest way to capture wind energy is the use of wind-electric turbine generator. Wind flows past the rotor, which spins it and the turbine rotor drives the shaft of the of a generator to make electricity. It is actually a pretty simple design.

Wind energy is proportional to the cube of the speed, this is demonstrated in the next section. Therefore, as one can imagine, wind speed is extrememly important and contrary to what some believe that strong winds are needed for wind turbines. Only moderate wind and steady wind is needed and is actually better suited then strong, gusty winds. Wind turbines start producing electricity when wind reaches around 12 to 15 miles per hour (5 to 7 meters per second) and peak at 30 miles per hour (13 meters per second). So areas that have sustained wind speeds between 10 to 15 miles per hour, seem like a good site for wind turbines.

Wind is classified by a system characterizing its power and is labeled by numeric's; 1, 2, 3, 4, 5, 6, and 7. Each one refers to a particular mean wind speed range, based on something called Rayleigh speed distribution, and hence energy flux. Table 9.1 shows these classifications.

9.2.2 Wind Energy flux

As indicated in the introduction, energy flux is extrememly important because it puts limitations on how much energy can be extracted from a par-

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[1] American Wind Energy Association, Wind Power Outlook 2007

Table 9.1: **Classes of Wind Speed at Heights of 10 m**

Wind Class	Speed m/s (mph)
1	$<$ 4.4 (9.8)
2	5.1 (11.5)
3	5.6 (12.5)
4	6.0 (13.4)
5	6.4 (14.3)
6	7.0 (15.7)
7	9.4 (21.1)

ticular source. First for the purposes of finding the kinetic energy of moving air molecules, lets say that the air is a giant cylinder (has the geometry of air molecules passing through the turbines blades) with the area, A, and thickness D. The volume is then just

$$V_{vol} = AD \tag{9.1}$$

Now lets say that ρ is the density of the air and we know that $\rho = M/V$. Also, the velocity of the air passing through the blades can be expressed as $v = D/T$ with T being the time it takes for the air of thickness D to pass through. Finally, we can find the energy flux starting from the basic kinetic energy expression;

$$\begin{aligned}
E &= \frac{1}{2}Mv^2 \\
E &= \frac{1}{2}(\rho V_{vol})v^2 \\
E &= \frac{1}{2}(\rho AD)v^2 \\
E &= \frac{1}{2}(\rho AvT)v^2 \\
E &= \frac{1}{2}\rho ATv^3 \qquad (9.2) \\
P_{ower} &= \frac{E}{T} = \frac{1}{2}\rho Av^3 \qquad (9.3)
\end{aligned}$$

and if we want the energy flux, we just divide by the area to get;

$$E_{flux} = \frac{1}{2}\rho v^3 \tag{9.4}$$

One can see, explicitly, that the energy flux is proportional to the cube of velocity. To find a typical energy flux, lets consider a very simple example. Suppose the wind is blowing at a constant velocity of 5.6 meters per second and the density of air is 1.225 kg per cubic meter. Using the equation above, the energy flux can be calculated to be 107 W/m^2. This value is typical of wind energy flux. However, no more then 16/27 of wind's kinetic energy can be extracted by a rotating horizontal-axis generator. This is known as the Betz limit and actual capture will be about 80% of it. Moreover, there is an average of 25% conversion efficiency and a 25% power loss caused by wakes and other factors. Therefore the final power density turns out to be between 5-20 W/m^2.

Lets take a look at the modern power densities of our high energy society in order to compare. Power densities range between 20-100 W/m^2 for houses, low energy offices, institutional buildings, and urban areas. Supermarkets and office buildings range from 200-400 W/m^2, industrial enterprises range from 300-900 W/m^2, and high rise buildings range can go up to 3kW/m^2. Fossil fuel societies can supply these power densities by diffusing concentrated energy flows as they produce fuels and thermal electricity with power densities of magnitudes higher than the power densities in buildings, factories, and cities.

As you can see wind's power density is much less then that of our current high energy density society. However, the low power density of wind isn't the main obstacle that can't be overcome. There is enough land available in the United States to support a capacity of about 500 GW. The problem that arises with wind is something that humans have no control over and that is its variability in space and time. We know that wind changes on a daily and seasonal basis, both of which is extrememly hard to predict. Wind flow normally doesn't peak during the time of high energy demand as well. Many densely populated areas with high electricity demand experience long seasonal periods of low wind speeds, which make wind almost unusable for harnessing. These factors limit winds ability to really compete with fossil fuels, it can only supplement a main energy source.

9.3 Water

Using water for useful work (hydropower)has been around as long as wind. It is one of the oldest sources of energy and was used thousands of years ago to turn a paddle wheel for purposes such as grinding grain. The first U.S. hydroelectric power plant opened on the Fox River near Appleton, Wisconsin, on September 30, 1882[2]. Since the source of hydropower is water, hydroelectric power plants must be located on a water source. Therefore, it wasnt until the technology to transmit electricity over long distances was developed that hydropower became widely used.

The basic principals of hydroenergy are very similiar to that of wind as will be shown. However, there are two systems for which water is used; *flow* and *fall*. Swiftly flowing water in a big river carries are great deal of energy, deriving its energy density is actually the same as wind as one can imagine. Falling water also carries a great deal of energy and in both instances turn turbines that spin a generator to produce electricity.

9.3.1 Basics of Hydropower

Water constantly moves through a vast global cycle, evaporating from lakes and oceans, forming clouds, precipitating as rain or snow, then flowing back down to the ocean. The energy of this water cycle, which is driven by the sun, can be tapped to produce electricity. Hydropower uses water as its fuel that is not reduced or used up in the process. Because the water cycle is an endless, constantly recharging system, hydropower is considered a renewable energy.

Water that falls from a higher elevation to a lower elevation through gravity contains energy. This energy can be captured near a waterfall or man made dams, which are artificial waterfalls. Dams increase the head (height of waterfall) and controls water flow. Water is released from the dam when electricity is needed. A hydroplant uses dams for the purpose of electricity generation and has three parts;

1. An electrical plant where the electricity is produced
2. A dam that increases the head and controls water flow
3. A reservoir where water can be stored

Electricity is produced when the dam opens up and water falls down a large tube called a penstock. At the end of the penstock the moving water turns a turbine that is connected to a generator. The electricity, from the generator, is then transferred to the local a utility company.

There are two factors that determine how much energy is produced at a hydroplant which are head and flow. As mentioned before, head is the

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[2] Energy Information Administration, official energy statistics from the U.S. Government

distance the water drops and flow is how much water moves through the system. A plant that has high head won't need as much flow to produce the same amount of electricity as a plant with a lower head.

One advantage that hydroplants have is its ability to store energy. The reservoir stores the water, which contains potential energy because of its elevation. Water is released when needed for electricity production or held back for future use. Also during the winter months, rain water can be saved for use in the summer time. This type of renewable energy is not variable and very predictable unlike wind.

Another type of use for water is flowing rivers, with the idea being very simiar to that of wind. The flowing water turns turbine blades, just like wind, which spin a generater that produces electricity. The general physics for wind and flowing water are the same except that the two densities are different.

9.3.2 Water Energy Flux

Just like wind, it is very useful to find the water energy flux. As mentioned before for a hydroplant, the power is determined from head and flow. The amount of energy that is released by lowering an object of mass m by a height h in the earths gravitational field is;

$$E = mgh \tag{9.5}$$

and as before the power is just

$$P_{ower} = \frac{E}{t} = \frac{mgh}{t} \tag{9.6}$$

Now we can make some substitutions to manipulate the equation to find a more usable form.

$$\begin{aligned} P_{ower} &= \frac{\rho V_{vol} gh}{t} \\ P_{ower} &= \rho \frac{V_{vol}}{t} gh \\ P_{ower} &= \rho A v g h \end{aligned} \tag{9.7}$$

with the area A being the cross-section of the penstock, v being the velocity of liquid water moved per unit time, and ρ being the density of water. Finally the energy flux is

$$E_{flux} = \rho v g h \tag{9.8}$$

To find the energy flux of a system set up from the flow of a body of water without changing the height, we use the same equations as we did for the wind energy flux. The only difference between the two being the density.

$$E_{flux} = \frac{1}{2}\rho v^3 \tag{9.9}$$

Again lets consider an example and for the purpose of this paper it will be very basic. Of course, every system is unique but one can get a ball park idea and compare with the standard fossil fuel systems. Lets consider a hydroplant having the following parameters;

- Penstock diameter of 13.2 meters
- Flow rate of 120 liters per minute
- Head of 30 meters
- Water Density of 1000 kg per m^3

Using equation 9.8, one will calculate a energy flux of 4.29 W/m^2. Normally the final power density is around 1 W/m^2. Comparing this to the current power density shows that it is much lower, even than wind. Typical final power densities for flowing rivers range between 10-50 W/m^2, which is a bit higher then wind as one would expect.

Not only is the power density low for hydroplants but, unlike wind, has some environmental impacts as well. Building reservoirs will cause change to the ecosystem downstream and in the reservoir. The water becomes warmer at the surface and has a lower oxygen content. This has a direct effect on the species, for some good and others bad. Therefore, the species that it is good for will thrive (smallmouth bass) and grow. While the species that these conditions do not favor (salmon) will dimish. Fluctuations in the water level will make it difficult for the shoreline area to support life and sediments can build up in the reservoir which will alter the water chemistry. Wildlife that depends on the shoreline for food, shelter, and other needs will be affected as well.

Recent studies also show that reservoirs are significant sources of greenhouse gas emissions due to the decaying vegetation (carbon dioxide and methane). So even though this seems like a clean renewable energy source, it turns out not to be. One last impact that hydropower systems have is mass population displacement, normally of poorer people. As dams being built became larger in dense populations, Asia, resettlement numbers surpass

100, 000 per reservoir. This is an incredible amount of people that have to relocate whether they want to or not.

The issues involving hydro generation outlined above weaken the case that this nonrenewable option can replace fossil fuels. Similiar to wind, it can and will only supplement a main energy source.

9.4 Nuclear

Nuclear Energy involves splitting heavy nuclei into lighter nuclei which release energy (fission) or combining lighter elements to heavier ones (fusion), normally hydrogen to helium. The fission process is used for the energy production in today's nuclear power plants and makes up about 16 % of the worlds electricity use.

Massive investments during the 1950s helped the nuclear industry emerge a major player for in electricity generation for industrial societies. It was predicted that nuclear was the future that could produce limitless power that would inexpensive. However, it was clear in the 1970s that there were some major issues that put a set back on this type of energy generation.

9.4.1 Nuclear Setbacks

The first setback came from the increased awareness of nuclear economics and system dynamics which caused a setback in new orders. Electricity was being generated in excess and not being absorbed by the predicted rise in electricity use. Once this was discovered, utilities stopped ordering new reators.

Next came two disastrous events which caused the public court to turn on nuclear energy and inturn new safety requirements were put on all plants. In 1979, the three mile-island plant located in Pennsylvania had a near meltdown. This caused evacuation of the local population and ceased all nuclear plants for further safety evaluation. Then in 1986 a melt down in a reactor located in Chernobyl, Soviet Union caused a radioactive cloud over parts of the Ukraine and western Europe. This meltdown showed the environmental catastrophe that could happen to future plants, which was devastating.

Finally, nations began to use their domestic nuclear programs as a decoy for weapons programs. As it will be shown in the next section, the nuclear reaction releases a tremendous amount of energy that can be used as a weapon. India set off a "peaceful nuclear explosion" in 1974, which was the wake up call to the international community. This caused nuclear energy programs to slow down in many of the nations and for good reason.

9.4.2 Nuclear Basics

When a neutron hits a large atomic nucleus, it forms two smaller nuclei releasing energy and neutrons. This is called fission and the neutrons that are released then trigger further fission. This goes on, something like a chain reaction. In nuclear power, this chain reaction is controlled and the energy released from the fission is used to produce steam to drive a turbine that generates electricity. Nuclear reactors normally use uranium-235 or plutonium-239, just like in uncontrolled reations (bombs), however the commercial reator grade nuclear fuel in not enriched enough for a nuclear explosion to take place.

The chain reaction is controlled through the use of materials that absorb neutrons. This makes sense because neutrons that are absorbed cannot take place in another reaction, hence slowing or controlling the process.

Lets take a look at how much energy is released from fission and compare to fossil fuels. A quick review of chemical reactions states that in an exothermic reaction, energy is released into the environment and in an endothermic reaction, energy is absorbed from the environment. During a chemical reaction, bonds are broken and new ones are formed. Breaking bonds is, of course, endothermic and bond making is exothermic.

Uranium-235 is the principle element used in nuclear reactors and when a neutron strikes it, the uranium absorbs it first to make uranium-236 (which is unstable). Then the atom fissions and can produce many different products. The following equations are two examples of this process;

$$^{235}U + N \longrightarrow 2N +^{92} Kr +^{142} Ba + Energy \tag{9.10}$$

$$^{235}U + N \longrightarrow 2N +^{92} Sr +^{140} Xe + Energy \tag{9.11}$$

The energy released (just going to state here) is shown in Table 9.2. So there is around 205 MeV released from the fission reaction. Also notice that two neutrons are released, which begin the chain reaction as mentioned above. Since we know that Uranium-235 $\approx$ 235 atomic mass units (amu), we know the energy density which turns out to be around $84,168,185$ MJ per kg. This seems like alot of energy, so now lets compare to fossil fuels.

Table 9.2: **Energy Released from on the fission of ^{235}U**

Distribution	MeV
Kinetic energy of fission fragments	167
Kinetic energy of fission neutrons	5
Energy of γ-rays	6
Sub-total of delayed energy	15
Neutrino energy	12

The combustion of fossil fuels reaction involves oxygen and is what we think of as a burning process. Fossil fuels are basically hydrocarbons, which are converted to carbon dioxide (greenhouse gas) and water in the process. In order to illustrate this lets look at a very simple fuel, methane. The equation is the following;

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \tag{9.12}$$

The energy released can be estimated from the bond energies and it turns out (not shown here) that there is about 9 eV released per mole . The molecules on the left hand side of the equation have a mass about 80 amu. The energy density turns out to be around 10.85 MJ per kg. This is an incredible energy difference, the ratio is $\approx 8 \times 10^6$!

If nuclear was purely looked at from the energy point of view, this could replace fossil fuels (unlike wind or hydro). However as mentioned previously there is so much other 'baggage' that nuclear carries along with it. Probably the most important is the fact that since so much energy is released, nations could use (and have) nuclear not for energy but for destruction.

9.4.3 Conclusions

Even though there is tremdous energy released from nuclear power and could supply the necessary energy needs for the world, a worldwide adoption of this option being the primary supplier would result in environmental and military disasters. With the rising number of nuclear power plants, the chances rise of severe number of accidents and unpreventable emergence of nuclear weapons.

9.5 Solar

Photovoltaics can be applied cost-effectively at all different scales, from small gadgets to utility generation, which is why this renewable is so promising. Of course there are groupings, depending on the type of application. The first group is the use of solar cells without any battery to store the energy. Some examples include, but not limited to, calculators, irrigation pumps, and distillers. Of course they can only operate while the sun is shining. The next type of grouping is the use of solar cells in connection with batteries, excess electricity is not wasted but stored and used at night. An example would be a yard light that stores electricity during the day so the light can work at night. These two type of small-scale single function systems comprise of about 15 percent of the PV capacity installed annually.

The next grouping is on a larger scale and is used to provide electricity to homes or other buildings that are off the utility grid. Traditionally, a home or building that is off the grid use gasoline powered generators but with solar modules there is no fuel delivery, operate silently, and work consistantly. Off grid type applications need battery storage so that electricity can be available during the night. Industrial and developing countries both use this type but it is more prevalent in developing countries where reliable grid electricity is hard to come by.

The on-grid group is the use of solar modules in conjunction with the grid. The solar modules are mounted to rooftops of homes or buildings and range from a few hundred watts to a few megawatts. During the day, the energy that is collected exceeds the energy needed so the excess energy is fed back into the grid. At night when there is no sunlight, the building or house uses energy from the grid as it normally would. The concept of net metering is appropriate because during the day, the meter moves negative and at night the meter moves positive. This application eliminates the need for a battery to store the energy collected. This group is driving the commercial growth today and the driving force in transforming fossil fuel society's into renewable society's.

Finally, very large scale centralized systems make up the last group. Utilities or industrial customers can take advantage of good solar characteristics to generate utility scale power. This is a small group of the current photovoltaic applications but should continue to grow in the future as solar cells become more effecient and cost effective. Realizing that about a third of the earth's surface is covered by sun-riched deserts, this application has the ability to generate a significant amount of energy.

The solar flux, which was introduced in the first part, turns out to be around 1353 W/m^2. However, much of this is absorbed by the atmosphere or reflected back into space. The solar flux that actually reaches the earth surface averages 168 W/m^2. Existing techniques allow the conversion to electricity with power densities of 20-60 W/m^2, which is far more then all the other renewables (besides nuclear).

Lets take a look at how much surface is needed to provide the planet with its current energy needs. As mentioned in Part I, 467×10^{18} joules were produced in the 2004. To convert this into power (joules/second), we divide by number of seconds in a year. The rate of energy produced is then 1.48×10^{13} W. Using the low end of the power density (20 W/m^2), we calculate the surface area needed to produce the power output of 2004.

$$\begin{aligned} A &= \frac{1.48 \times 10^{13}}{20} \\ A &= 7.4 \times 10^{11} m^2 \end{aligned} \tag{9.13}$$

If we assume that the earth is a perfect sphere, the total surface area is just;

$$\begin{aligned} A &= 4\pi(R)^2 \\ A &= 4\pi(6379km)^2 \\ A &= 5.11 \times 10^{14} m^2 \end{aligned} \tag{9.14}$$

Looking at the ratio between the the two, we find that if 0.145% of the earths surface was covered with solar cells today's energy needs would be satisfied using today's technology! Now if we could increase the efficiency of the solar cells to an upper value of 40%, only 0.043% of the earths surface would be needed.

9.6 Other Renewables

Of course there are some other renewable options that have not been discussed in this chapter, which include biomass, geothermal, and fuel cells (probably some others as well). Although some may argue that each one is the future of energy, they aren't in my opinion.

Biomass is obtained from various forms of plant and animal waste (wood and dung being the leaders). Most of biomass is released from burning and the power densities are less then 1W/m^2. With this low energy density and the fact that most likely burning will be needed, biomass' potential impact on the future of energy looks grim.

Geothermal electricity does have one advantage over wind and solar, the fact that it is stable. This makes it a dependable source of energy, however it is geographically limited. The locations close enough to the earths surface where heat is found is very tiny. This alone excludes it from replacing fossil fuels.

Fuel cells are devices that combine hydrogen with oxygen to generate electricity, producing heat and water (zero carbon 'footprint'). Explicitly the chemical reaction is;

$$2H_2 + O_2 \longrightarrow 2H_2O + energy \tag{9.15}$$

This process generates electricity much more efficient then burning fossil fuels and the by products can be used in other applications. Also fuel cells lack moving parts, which increase their lifespan. Fuel cells, on the surface, look like a viable option however the environmental benefits disappear when the source of hydrogen is considered. Almost all of the worlds hydrogen comes from reforming fossil fuels so there is no environmental benefit to make the transition.

Chapter 10

Government Role

Governments play a important role when it comes to electricity systems. Up until the late 1980's, electricity was either government run or heavily regulated in the industrial world. Prices and investments were overseen by the government and market forces had little or no impact. Since then, industrial countries have restructured their electricity systems by injecting competition into the energy sector.

10.1 Noncompetitive Electricity Systems

Electricity was a monopoly (either tightly run private company or public agency), it used to make sense to have one company doing the work. The argument was simply that electricity should be reliable and cheap. Therefore, governemnt should control or regulate the system.

In the U.S., electricity was provided by electrical utilities that were owned by private firms and were responsible for generation, transmission, and distribution. They were regulated by the state governments and the main regulation was the prices that they were allowed to charge. However, there were some other decisions that went to the regulators as well. This system did provide reliable electricity but there were some drawbacks. New technology, being innovative, and offering new products were surpressed by the nature of no compitition. Therefore, old technology dominated with little or no incentive for research and development.

Changes in this system started to take place in 1978 when the (in the U.S.) government passed a law requiring utilities to purchase electricity from other companies. Before this law, it was impossible for other companies to crack the electricity generation buisness because utilities controlled everything. It didn't make sense for the utilities to buy electricity because they made their electricity. A simple argument that if potential electricity generation companies could make electricity cheaper, then why shouldn't the utilities buy. So the U.S. government passed a law to do force utilites to buy elsewhere if it made sense. This law was called PURPA, the Public Utility Regulatory Policies Act.

At about this same time, the technological advance of the natural gas fired turbine hit the scene. This type of turbine made it possible to generate electricity less then the utilities. The centralized, regulated utility structure started to look outdated as more of the natural gas industrial sized power plants were built. This added political pressure for large industrial company's to produce their own electricity, as it was cheaper to make and use on site then buy from the utilities.

Since utilities were regulated by states, there were some large price differences from state to state which added to the already growing polical pressure for a change. For states where nuclear power was, the electricity cost more and caused industry threaten to move to another state where electricity was cheaper.

Finally, there was a global trend toward privatization. The cause for this privatization varied from country to country but the overall theme was that customers were unhappy with the service provided. Since governments basically controlled the the electricity, all the dissatisfaction was directed toward them and change was demanded.

10.2 Today's Electricity Systems

Today economics, because of the privitization of electricity, is the driving force of renewables. Government, however, is still involved and has an important role. For example, govenment policy tools in Japan and Germany have promoted the use of photovoltaic's. If it wasn't for the policy, then the PV industry wouldn't be thriving as it is today in those country's.

The traditional energy industries, fossil fuels, right now are heavily subsidized in the world. The money that is given to these industries from the government offset the real costs of generation and keep non-tradional sources (photovoltaics) from cracking the market. Therefore, this encourages consumers to use fuel and electricity more inefficiently.

The subsidies have been difficult to eliminate because of the traditional energy political influence. Of course this makes unsubsidized photovoltaics or renewables much less desirable. Until the subsidies cease, photovoltaics must be much more economically attractive then fossil fuels for market adoption. So if subsidies aren't going to 'go away' anytime soon, which they probably won't, can there be other ways government can encourgage renewables? Sure there are a few ways, first create incentives to install renewable energy and second penalize fossil fuel energy sources in monetary value for the amount of pollution.

10.2.1 Incentives

Program incentives that have stimulated the use of renewables and photovoltaics have been net metering, feed-in-tariffs, and rebates to name a few. Some countries have been more successful then others by employing combinations of incentives, some examples are Japan and Germany.

Feed-in tariffs require a utility company to accept power from a renewable source at a set price over a certain time frame. The price will vary depending on the actually renewable technology, time of day, etc. and is normally in cents per kWh. Germany has successfully used this approach. Germany began to develop its solar energy infrastructure in the mid-1990's from a program called the Hundred Thousand Rooftops program. From 1999 to 2003 this program generated huge interest by offering 50 eurocent per kWh feed-in tariff for a twenty year period. The photovoltaic industry has skyrocketed and it is expected to continue this way, as Germany has begun phasing out its subsidies for coal and nuclear power. This will push the photovoltaic industry to make up any energy gaps that might be lost, stimulating research and increasing solar cells.

Rebates are another incentive that lower the initial installation of renewables, primarly photovoltaic's. U.S. states and other countries employ this program which normally pay consumers some cost per peak kW. The U.S. federal government doesn't necessary support this program but alot of states are starting to adopt it and this is the force driving the growth in the U.S. photovoltaic grid-tied system. For example New Jersey offers up to half the cost of the initial installation of solar panels on rooftops.

As mentioned in the previous chapter, there is a concept of net metering. Once a consumer can connect their photovoltaic system to the grid, they need to be compensated for providing energy back to the grid. Net metering does just this and actually both the utility and end-consumer benefit.

Utilities can take the expensive energy generated during the day from the PV system (charge a fixed rate for energy flowing back to the grid) and reduce it at cheap night time costs. The end consumer benefits as well for the obvious reason.

10.2.2 Penalizing

Some governments can employ an adverse incentive to use fossil fuels and that is by penalizing the pollution it generates. Emission taxes are used to penalize emitters of pollution and greenhouse gases which affect how much and what type of energy is used. These taxes provide an incentive for fossil fuel plants to clean up their pollution by employing control technology. However, it is in my opinion that these programs aren't that effective for reasons that are beyond this paper.

10.2.3 Japan

Japan is a country that has scarce natural resources, especially energy and are dependent on imports (fossil fuels). Japan, because of this, has experienced very high electricity prices. This has prompted government policy to develop alternative energy sources though subsidies. They started a program called the Seventy Thousand Roofs program in 1995, which initially provided 50% subsidy on grid-tied photovoltaic systems. This made the cost of using electricity generated from PV systems competitive with electricity generated from traditional sources. This provided rapid growth in the research and development, manufacturers, and installation of photovoltaics. These systems are now providing electricity at or below the average residential price of $0.21 per kWh. Subsidies have been tapered off to keep it competitive with the conventional energy sources! Now not only have Japan's reliance on fossil fuel imports diminished but their technical expertise in PV systems are being exported to countries like brazil and mexico. Japans government has made the nation the world leader in PV technology through PV policy.

10.2.4 Conclusion

Governments play large roles when it comes to the energy sector. Take a look at Japan and Germany who, through government policy, are pushing photovoltaics mainstream and developing the technology that is needed in order to make the complete transition. In the U.S., the federal government is not doing much about solar promotion, they do have some tax credits but still the states are doing much of the work.

Chapter 11

The Future of Photovoltaics

The current energy society will have to transition to a new one, that is a fact. This transition is a shift away from the fossil fuels as they become scarce and damaging to the environment. The future energy society will be more evolved in the sense that energy will be in more useful forms like electricity and be more distributed. Photovoltaics naturally fulfill this future society, looking at Japan and Germany. It is much more evenly distributed then any other renewable so that there will be no need to have large centralized energy sources. With large centralized energy sources; there are power outages, monopoly's, greater security risks, etc. This doesn't happen with a more distributed energy source.

This transition is starting to happen today because photovoltaic electricity has started to become cost effective in large grid-tied markets (Japan). While Japan's high electricity prices provide the natural motivation to develop solar solutions, it was only strong policy that pushed Japan to develop the photovoltaic industry. Markets with better solar resources will soon start popping up, probably in southwest U.S. and southern Europe, that will compete with tradional grid based electricity.

The tradional energy sector do perceive renewable or distributed energy as a threat, however the learning rate for photovoltaic technology cannot be easily be slowed. The growth of the photovoltaic industry over the last decade has basically occured by the Japanese and German microelectronics manufacturers. However, in the U.S., General Electric bought AstroPower, which used to be the largest solar cell manufacturer and is creating reasearch centers for further development of renewable technologies. Whether the big boys of the tradional energy sector like it or not, photovoltaics are becoming more and more commercial and it would probably be in their interest to start the transition themselves by developing these technologies instead of trying to surpress them.

The world is embarking on a revolutionary change from the large centralized fossil fuel energy to renewable (mostly photovoltaic) distributed energy. Solar energy will change the shape of the industrial and developing countries and will enable everybody to be on equal energy footing. There won't be anymore tradeoff's between current standards of living and environmental damage. Fossil fuels should be an artifact of the past remembered for its troubled history, as there should be no need for political tension as far as energy is concerned in the future.

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