A spectroscopic study of strain-balanced InGaAs/GaAsP quantum well structures as absorber materials for hot carrier solar cells

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I hereby declare that the work presented in this document is my own, except where specifically described in the text.

The work of others has been acknowledged and list of references is provided.
Abstract

In this thesis, five intrinsic loss mechanisms which fundamentally limit solar energy conversion efficiency are identified. The three dominant mechanisms are thermalisation loss, below $E_g$ loss and Boltzmann loss. Targeting these three losses through alternative device design is the only way substantial efficiency enhancement might be achieved. The hot carrier solar cell targets these dominant mechanisms and hence has a theoretical limiting efficiency, under maximum solar concentration, in excess of 80%. Despite clear efficiency advantages, a hot carrier solar cell has never been experimentally demonstrated because two key development challenges remain: energy selective contacts and absorber materials which maintain a hot carrier distribution under realistic levels of incident solar irradiation.

In this study, strain-balanced InGaAs/GaAsP QW structures with a range of QW parameters were characterised spectroscopically in order to determine the suitability of this material system as a hot carrier absorber. In a deep, wide well sample, a temperature gradient between the carrier distribution and the surrounding lattice of 150 K was demonstrated using continuous wave photoluminescence spectroscopy. This technique was also used to calculate a thermalisation coefficient for each sample, allowing for comparison with other hot carrier studies.

Time resolved photoluminescence measurements were used to identify cooling pathways occurring in this material system. Bi-exponential cooling behaviour was observed, indicating that two different mechanisms with different characteristic cooling lifetimes were dominating carrier cooling. In the deep, wide well sample it was determined that peak LO phonon distribution temperatures of at least 500 K above that of the surrounding lattice would be required to produce the observed carrier cooling.
I would like to start by acknowledging Ned Ekins-Daukes for his inspirational supervision throughout my PhD. Thanks to Ned’s careful guidance and depth of PV knowledge, my PhD has been an truly incredible learning experience.

I have been lucky enough to travel all over the world with this project and have profoundly benefitted from the insights and enthusiasm of the individuals I met along the way. The beautiful samples used in this study were grown by Sugiyama-sensei and his team at the University of Tokyo. Without their skills and experience none of the results obtained in this study would have been possible. I was also privileged to spend time characterising samples with Kita-sensei and his students at the University of Kobe, Murad Tayebjee, Raphael Clady and Tim Schmidt at the University of Sydney, and Jean-François Guillemole and Arthur Le Bris at IRDEP in Paris. I am hugely grateful to these groups for dedicating many dark hours in the spectroscopy lab to this project and taking the time to pass on a wealth of spectroscopy knowledge to me. I would like to thank all my international collaborators for being such gracious hosts, introducing me to local delicacies and making sure I had a fantastic time on my travels.

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I would like to acknowledge my parents of their unwavering support, both moral and practical, throughout my time as a student at Imperial. Finally, I would like to acknowledge Jan for evangelising me in the doctrine of Linux, tirelessly listening to my syntax related emergencies and carrying my laptop into college!
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Abbreviations

$\alpha(E)$ absorption coefficient
$\Delta T$ $T_{eh} - T_L$
$\epsilon(E)$ emissivity
$h\omega_{LO}$ LO phonon energy
$T_C$ cell temperature
$T_{eh}$ carrier distribution temperature
$T_{LA}$ LA phonon distribution temperature
$T_{LO}$ LO phonon distribution temperature
$T_L$ lattice temperature
$T_S$ Sun’s temperature
$\mu$ chemical potential
$\Omega$ solid angle of emission, $\Omega_S = 1.6 \times 10^{-5}$ and $\Omega_C = \pi$.
$\tau_{eh-LO}$ carrier-LO phonon scattering lifetime
$\tau_{LO-LA}$ LO-LA phonon scattering lifetime
$\tau_{th}$ characteristic carrier cooling lifetime
$\alpha(E)$ absorptivity
$C_{ch}$ carrier specific heat
$C_{LO}$ LO phonon specific heat
$D_e(E)$ electron density of states
$D_h(E)$ hole density of states
$E_f$ Fermi energy
$E_g$ Energy bandgap
$f_c(E, T, E_f)$ electron fermi distribution
$f_v(E, T, E_f)$ hole fermi distribution
$h$ Planck’s constant, $h = h/2\pi$
$J_{opt}$ optimal operating current
$J_{SC}$ short circuit photo-current
$k$ Boltzmann’s constant
$m_e^*$ electron effective mass
$m_h^*$ hole effective mass
$n_e(E, T, E_f)$ density of electrons in the conduction band
$n_D$ background doping density
$n_{eh}$ carrier density
$n_i$ intrinsic carrier density
$n_{ph}(E, T, \mu, \Omega)$ the photon flux emitted from a black or grey body per unit energy interval
$n_h(E, T, E_f)$ density of holes in the valence band
$P_{abs}$ absorbed power
$P_{th}$ carrier energy loss rate
$V_{OC}$ open circuit voltage
$V_{opt}$ optimal operating voltage
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tr>
<td>As</td>
<td>arsenic</td>
</tr>
<tr>
<td>B</td>
<td>bio-molecular rate of recombination</td>
</tr>
<tr>
<td>CWPL</td>
<td>continuous wave photoluminescence</td>
</tr>
<tr>
<td>DBR</td>
<td>distributed Bragg reflector</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>Ga</td>
<td>gallium</td>
</tr>
<tr>
<td>Ge</td>
<td>germanium</td>
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<tr>
<td>HCSC</td>
<td>hot carrier solar cell</td>
</tr>
<tr>
<td>In</td>
<td>indium</td>
</tr>
<tr>
<td>LA</td>
<td>longitudinal acoustic</td>
</tr>
<tr>
<td>LO</td>
<td>longitudinal optical</td>
</tr>
<tr>
<td>MJ</td>
<td>multijunction</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metalorganic vapour phase epitaxy</td>
</tr>
<tr>
<td>MQW</td>
<td>multiple quantum well</td>
</tr>
<tr>
<td>NIR</td>
<td>near infra-red</td>
</tr>
<tr>
<td>P</td>
<td>phosphorus</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>PLE</td>
<td>photoluminescence excitation</td>
</tr>
<tr>
<td>PMT</td>
<td>photo-multiplier tube</td>
</tr>
<tr>
<td>ps</td>
<td>picosecond</td>
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<tr>
<td>PV</td>
<td>photovoltaics</td>
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<tr>
<td>Q</td>
<td>thermalisation coefficient</td>
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<tr>
<td>QW</td>
<td>quantum well</td>
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<tr>
<td>Si</td>
<td>silicon</td>
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<tr>
<td>TCSPC</td>
<td>time correlated single photon counting</td>
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<tr>
<td>ti-sapph</td>
<td>titanium sapphire laser</td>
</tr>
<tr>
<td>TO</td>
<td>transverse acoustic</td>
</tr>
<tr>
<td>TO</td>
<td>transverse optical</td>
</tr>
<tr>
<td>TRPL</td>
<td>time resolved photoluminescence</td>
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<tr>
<td>TTS</td>
<td>transit time spread</td>
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Publications

Book Chapter


Journal article

  13 citations as of 26/06/2012

Conference Proceedings

  Oral presentation
  Invited talk
  Oral presentation

• L. C. Hirst and N. J. Ekins-Daukes (2010), Quantifying intrinsic loss mechanisms in solar cells: Why is power efficiency fundamentally limited? Proc. SPIE 7772, 777211, DOI:10.1117/12.860681
  Oral presentation

  Poster presentation

• L. C. Hirst and N. J. Ekins-Daukes (2009), Thermodynamics of third generation solar cells. Proceedings of the 5th PVSAT
  Oral presentation

Prizes


• Runner up, Best Overall Conference Paper, 5th PVSAT (2009).
Light can be directly converted into electricity in solar cells via the photovoltaic effect. The primary application of photovoltaic devices is to generate electricity from solar energy hence, the parameters of the solar resource define the requirements of a solar energy conversion system.

1.1 Solar resource

Light is quantised into energy packets, or particles, called photons. The Sun emits light over a broad range of photon energies including ultraviolet (UV), visible and infra-red (IR) light. This radiation can be approximated as the emission from a black body of temperature 6000 K.
1.2 The photovoltaic effect

1.1.1 Black body radiation

A black body is a body which absorbs all wavelengths of light. No light is reflected and therefore, at low temperature, it appears black. Emission from a black body is temperature dependent and at high temperature a black body will emit a spectrum of photon energies which spans the visible range, and therefore it will appear white. The Sun is an example of a high temperature black body. Planck’s Law of radiation, equation 1.1, quantifies photon flux, emitted through the surface of a black body into a defined solid angle, per unit area, per unit energy interval.

\[
n_{ph}(E, T, \Omega) = \frac{2\Omega}{c^2 h^3} \frac{E^2}{\exp[E/kT] - 1}
\]  

(1.1)

\(E\) is photon energy, \(T\) is the temperature of the emitting body, \(\Omega\) is the solid angle of emission, \(c\) is the speed of light, \(h\) is Planck’s constant and \(k\) is Boltzmann’s constant. Planck’s law of radiation provides a good approximation of incident solar radiation, however many other factors such as daily and annual cycles and atmospheric absorption and scattering will have a significant effect on the spectrum observed at a particular location and hence real world device performance. Many of these factors are highly site specific and will be very important in evaluating the suitability of certain photovoltaic device designs and the operating capacity of a solar power station. Terrestrial and extra-terrestrial spectra used to characterise real world solar cells are shown in figure 1.1 alongside a 6000 K black body spectrum.

1.2 The photovoltaic effect

Photovoltaic conversion will only occur in a device exhibiting two essential features. Firstly, a solar cell must absorb solar radiation, converting the Sun’s heat energy into chemical potential in the device. When light is incident on matter it can provide sufficient energy to excite atomic electrons into higher energy states. In the case of semiconductor materials, such as silicon or germanium, this energy allows electrons to escape from their bound state and become free charge carriers, moving along a path of least resistance.

Secondly, a solar cell must exhibit asymmetric electrical resistance. Asymmetry in the material
allows negatively charged free electrons to move to one side of the material, leaving the opposite side positively charged. As electrons accumulate at one terminal a potential which opposes the motion of the charge carriers is generated. The generated potential defines the voltage across the device. This is called the photovoltaic effect (Becquerel, 1839).

When the terminals of a solar cell are short circuited no charge will accumulate at the terminals as electrons will flow uninhibited across the short circuit to the opposite terminal. In this instance the maximum current will flow but no voltage will be generated. When a load resistance is placed across the terminals electrons will collect at the terminals generating a voltage across the device but restricting current flow. In this way, a solar cell can supply useful electrical work to a load resistance.

### 1.3 Absorption profile of a solar cell

A solar cell must have an absorption profile which complements the broad solar spectrum. The monochromatic absorption of a single atomic transition is a poor match for the Sun’s...
1.3 Absorption profile of a solar cell

Figure 1.2: a) Emission from a black body with $a(E) = \epsilon(E) = 1$ and $T = 6000\,K$, $T = 5000\,K$ and $T = 4000\,K$. b) Emission from a grey body with step like absorption and emission profile shown in c).

spectrum. A material exhibiting a broad continuum of electron energy levels is required to access a large portion of the available irradiance. Metals with rough surfaces behave like black bodies. They have a broad continuum of electronic energy levels, hence are able to absorb most of the solar spectrum. Despite being good absorbers, metals do not make efficient PV materials because of a process called thermalisation, in which excited electrons lose energy to the surrounding atomic lattice.

Above absolute zero atoms in a solid vibrate. These vibrations are quantised into energy packets called phonons. Phonons and electrons in a solid interact, exchanging energy and momentum, allowing photo-excited electrons to return to their original ground state via the continuum of electronic levels. These interactions occur on an extremely rapid time scale ($<\,\text{ps}$) preventing the electron populations forming an excited steady state from which useful energy can be extracted. A gap in available electronic states is required to halt phonon emission and prevent excited electrons cascading through energy levels back to their original state. This can be achieved in a grey body with a threshold absorption profile as shown in figure 1.2. A grey body, like a black body, has an emission profile defined by the temperature of the emitting body, however, in a grey body this profile also contains an energy dependent emissivity term, $\epsilon(E)$. Such a material will emit light according to equation 1.2, which is the
1.4 Semiconductors

Semiconductors are grey bodies. They have a continuum of electronic energy levels which is interrupted by a forbidden region, called the energy bandgap ($E_g$). As isolated atoms come together in a solid, their discrete atomic energy levels split into degenerate bands of allowed electronic states, figure 1.3 (Yu and Cardona, 2005). The valence band describes the highest filled band of electronic states at absolute zero. The energy band directly above is called the conduction band. Partial occupation of the conduction band is required for a material to behave as an electrical conductor. When all valence band states are fully occupied with...
1.4 Semiconductors

electrons no current can flow. This is because there are no vacant states for the electrons
to move into. When an electron is promoted into the conduction band it leaves behind a
positively charged vacancy. It is convenient to consider this vacancy as a particle called a hole.
The conduction band is no longer empty and the valence band is no longer full, and hence a
current will flow under an applied field.

The separation between conduction and valence bands is defined as $E_g$ and this controls the
absorption and emission threshold of the material. Photons with energy greater than $E_g$ can be
absorbed by the material. In the case of metals, conduction and valence bands overlap, making
them good electrical conductors and giving them an uninterrupted continuum of electronic
energy states. An insulator has a large energy bandgap (>3 eV) and therefore practically no
electrons occupy the conduction band at room temperature. The large forbidden energy region
also prevents the absorption of most of the solar spectrum because most incident photons
will not have sufficient energy to excite an electron into the conduction band. Semiconductor
materials have an energy bandgap in the region 0.5 to 3 eV. This absorption threshold balances
the requirements of broad spectral absorption and energy discontinuity, to make efficient solar
converters. At room temperature in the dark most semiconductors are highly electrically
resistive. Under illumination however, electrons are promoted to the conduction band, allowing
the material to behave as a conductor. This is known as photo-conductivity.

1.4.1 Energy band structure

The minimum energy state in the conduction band occurs at the conduction band edge ($E_c$).
Electrons in this energy state have zero kinetic energy. Electrons with kinetic energy occupy
energy levels higher in the conduction band. The reverse is true for holes in valence band
states.

The energy ($E$) and momentum ($p$) of free electrons is described by the parabolic relationship
shown in equation 1.3, where $m$ is the mass of the particle.

$$E = \frac{p^2}{2m} \quad (1.3)$$
1.4 Semiconductors

In a crystalline structure, the motion of electrons and holes is affected by the periodic potentials around the atoms. An expression analogous to equation 1.3 can be applied to carriers in a solid, accounting for the crystalline structure with an effective mass term (Yu and Cardona, 2005). This approximation is only valid for low values of momentum, close to the conduction band edge. Equation 1.4 describes the energy of conduction band electrons with effective mass $m_e^*$. Equation 1.5 describes the energy of valence band holes with effective mass $m_h^*$.

$$E = E_c + \frac{p^2}{2m_e^*} \quad (1.4)$$

$$E = E_v - \frac{p^2}{2m_h^*} \quad (1.5)$$

Momentum is defined along the crystal axes of the structure and therefore it is possible for the kinetic energy minima, $E_c$ and $E_v$, to occur at a non-zero momentum value relative to this axis. It is also possible for $E_c$ and $E_v$ to occur at different momenta relative to each other. Equations 1.4 and 1.5 describe electrons and holes in direct bandgap semiconductors, where $E_c$ and $E_v$ occur at the same momentum, figure 1.4a. GaAs is an example of a direct bandgap material.

Indirect bandgap semiconductors have $E_c$ and $E_v$ at different momentum values, figure 1.4b. The energy-momentum relations for electrons and holes in indirect materials are given by equations 1.6 and 1.7 respectively. The momentum shift between the band edges and zero crystal momentum is given by $p_{0c}$ and $p_{0v}$. Silicon and germanium are examples of indirect bandgap materials.

$$E = E_c + \frac{(p - p_{0c})^2}{2m_e^*} \quad (1.6)$$

$$E = E_v - \frac{(p - p_{0v})^2}{2m_h^*} \quad (1.7)$$

When a photon is absorbed in a semiconductor, promoting an electron from the conduction band into the valence band, momentum must be conserved as well as energy. Photons have effectively zero momentum with respect to electrons and therefore indirect transitions require
1.4 Semiconductors

Figure 1.4: a) Electronic band structure for a direct bandgap semiconductor. $E_c$ and $E_v$ both occur at crystal momentum $p = 0$. Photons with energy $E_g$ can promote electrons into the conduction band without a change in momentum (dashed line). b) Electronic band structure for an indirect bandgap semiconductor. $E_c$ does not occur at the same crystal momentum as $E_v$. A change in momentum is required for a photon of energy $E_g$ to promote an electron into the conduction band (dashed line). This extra momentum can come from a lattice phonon.

momentum from another source. A lattice phonon can provide sufficient momentum to enable the transition however, the requirement of an additional particle reduces the likelihood of the interaction occurring. Photon absorption and emission from indirect transitions are suppressed relative to direct transitions.

1.4.2 Carrier populations in semiconductor materials

The population of carriers in a semiconductor is described by a density of states function, which defines the electronic states in the material system, and a distribution function which determines the occupation of those states according to Fermi-Dirac statistics.

1.4.2.1 Density of electron states

The density of electron states $D_e(E)$ can be derived from the uncertainty principle, equation 1.8, where $h$ is Planck’s constant.

$$\Delta p \Delta x = h$$  \hspace{1cm} (1.8)
For two electron states to be distinct they must differ in momentum and space by $\Delta p$ and $\Delta x$ respectively, hence the volume in momentum space ($\Delta p^3$) occupied by each state can be described as shown in equation 1.9, where $V = \Delta x^3$.

$$\Delta p^3 = \frac{\hbar^3}{\Delta x^3} = \frac{\hbar^3}{V}$$ (1.9)

The number of electron states ($N_e(p)$) with momentum less than $|p|$ is given by dividing the volume of a sphere in phase space of radius $|p|$ by the volume occupied by each state, as shown in equation 1.10. An additional factor of two is included because two electrons of opposite spin can occupy each state.

$$N_e(p) = 2 \left( \frac{4\pi |p|^3}{\hbar^3/V} \right)$$ (1.10)

The parabolic energy-momentum relationship, equation 1.4, is then substituted to give the number of electronic states with energy less than $E$, equation 1.11.

$$N_e(E) = 2 \frac{4\pi (2m^*_e(E - E_c))^{3/2}}{\hbar^3/V} = \frac{8\pi (2m^*_e)^{3/2} V}{3\hbar^3} (E - E_c)^{3/2}$$ (1.11)

The density of electron states per unit energy interval, in unit volume ($V = 1$) is determined by taking the derivative of $N_e(E)$ with respect to energy, equation 1.12.

$$D_e(E) = 4\pi \left( \frac{2m^*_e}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2}$$ (1.12)

A similar equation can be derived for the density of hole states, equation 1.13 (Sze, 2002).

$$D_h(E) = 4\pi \left( \frac{2m^*_h}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2}$$ (1.13)

### 1.4.2.2 Occupation of electron states

At absolute zero electrons populate the lowest available energy levels, according to the Pauli exclusion principle, with each state supporting two electrons of opposite spin. As temperature increases electrons acquire kinetic energy and are able to occupy higher energy levels. Electrons are fermions and as such the probability of an electron state being occupied is described by
the Fermi-Dirac distribution, equation 1.14. The Fermi-level \( E_f \) is the energy at which half of all states are occupied.

\[
f_e(E, T, E_f) = \frac{1}{\exp[(E - E_f)/kT] + 1} \tag{1.14}
\]

A hole describes the absence of an electron and hence the distribution function of holes is given by equation 1.15.

\[
f_h(E, T, E_f) = 1 - f_e(E, T, E_f) = \frac{1}{\exp[(E_f - E)/kT] + 1} \tag{1.15}
\]

### 1.4.2.3 Carrier density

Multiplying the Fermi-Dirac distribution by the density of electron states gives an expression for the density of electrons in the conduction band \( n_e(E, T, E_f) \), equation 1.16. The density of holes in the valence band \( n_h(E, T, E_f) \) is similarly derived, equation 1.17.

\[
n_e(E, T, E_f) = D_e(E)f_e(E, T, E_f) = 4\pi \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \frac{(E - E_c)^{1/2}}{\exp[(E - E_f)/kT] + 1} \tag{1.16}
\]

\[
n_h(E, T, E_f) = D_h(E)f_h(E, T, E_f) = 4\pi \left( \frac{2m^*_h}{\hbar^2} \right)^{3/2} \frac{(E_v - E)^{1/2}}{\exp[(E_f - E)/kT] + 1} \tag{1.17}
\]

Figure 1.5 shows the density of states, the Fermi-Dirac distribution and the density of carriers.

The total number of conduction band electrons is calculated by integrating \( n_e(E, T, E_f) \) with respect to energy over the energy range \( E_c \rightarrow \infty \), equation 1.18 (Würfel, 2009). To allow an analytical solution to this integration the +1 in the denominator of the Fermi function must be ignored. This is a valid approximation for non-degenerate semiconductors, for which \( E_f < E_c - 3kT \) and carriers form an ideal gas. This approximation is valid for semiconductors...
1.4 Semiconductors

Figure 1.5: The electron population in the conduction band \(n_e(E, T, E_f)\) (green lines) is the product of the density of electron states \(D_e(E)\) (black lines) and the Fermi-Dirac distribution \(f_e(E, T, E_f)\) (red lines). The hole population in the valence band is similarly defined. Solid lines refer to electrons and dotted lines refer to holes.

at 300 K under one Sun illumination. The approximation breaks down for devices under high concentration (> 100 Suns). The total number of electrons in the conduction band is given by equation 1.18.

\[
n_e(T, E_f) = \int_{E_c}^{\infty} n_e(E, T, E_f) \, dE \\
= N_c \exp\left(-\frac{E_c - E_f}{kT}\right)
\]

where

\[
N_c = 2 \left(\frac{2 \pi m_e^* kT}{\hbar^2}\right)^{3/2}
\]

The total number of holes in the valence band is given by equation 1.20.

\[
n_h(T, E_f) = \int_{E_v}^{\infty} n_h(E, T, E_f) \, dE \\
= N_v \exp\left(-\frac{E_f - E_v}{kT}\right)
\]

where

\[
N_v = 2 \left(\frac{2 \pi m_h^* kT}{\hbar^2}\right)^{3/2}
\]
The number of conduction band electrons and valence band holes is a function of temperature and Fermi level. Varying the temperature changes the shape of the Fermi distribution. Changing the Fermi level shifts the Fermi distribution in energy, without effecting the shape of the function. The Fermi distribution will be shifted in a semiconductor under illumination and also with the addition of impurity atoms to the semiconductor lattice.

1.4.3 Doping

Doping is the process of replacing atoms in a semiconductor lattice with impurity atoms which have a different number of valence electrons, figure 1.6. Donor impurity atoms have more valence electrons than necessary to bond with the host semiconductor. The impurity atom is bound to the lattice with strong covalent bonds fixing the position of the atom. Additional electrons are not required for bonding and therefore only experience a weak Coulomb attraction to the donor atom. This is easily overcome thermally and at 300 K almost all donor atoms are positively ionised. A semiconductor doped in this way is called n-type as negative electrons are the principal charge carriers in this material. The increase in conduction band electron population is characterised by a shift in $E_f$ towards the conduction band edge, figure 1.7. Acceptor atoms have too few electrons to bond with the host semiconductor lattice. The impurity bond is completed by removing a valence electron from the surrounding structure, populating the valence band with additional holes. This is known as a p-type semiconductor as positively charged holes are the principal charge carriers. This increase in valence band hole population can be described by a shift in $E_f$ towards the valence band edge, figure 1.7.

1.5 pn junction

In order for a semiconductor to start behaving like a solar cell, the device requires some built-in resistive asymmetry to draw excited carriers into an electrical circuit. A pn junction is a diode formed from layers of oppositely doped semiconductor material which forces excited carriers to flow in one direction. When n-type and p-type semiconductor materials are brought together in a pn junction the random thermal motion of the carriers allows them to diffuse across the
Figure 1.6: a) A donor atom (grey) in a semiconductor lattice. The additional electron makes the material n-type. b) An acceptor atom (black) in a semiconductor lattice. The electron vacancy makes the material p-type.

Figure 1.7: Density of states functions (black lines), Fermi-Dirac distributions (red lines) and the density of carriers (green lines) are shown for n-type and p-type doped semiconductors. Solid lines refer to electrons and dotted lines refer to holes. In an n-type semiconductor the introduction of donor atoms shifts the $E_f$ towards the conduction band. $E_f$ shifts towards the valence band in a p-type semiconductor.
junction along concentration gradients. This is a result of the greater electron population in the n-type semiconductor and the greater hole population in the p-type semiconductor. The impurity ions are fixed in the semiconductor lattice and so get left behind, creating an electric field across the junction. This field opposes the motion of the carriers, causing carriers to drift back across the junction. Equilibrium is achieved when diffusion and drift mechanisms balance, establishing an area of transition across the junction called the depletion region. $E_f$ is constant across the junction under equilibrium conditions creating a potential step in conduction and valence band edges, referred to as built-in voltage. Over the depletion region the gradient of carriers forms a smooth energy profile across the junction, figure 1.8.

1.5.1 Solar cells in circuits

The photovoltaic effect requires both photo-current generation and asymmetric electrical resistance and as such, a solar cell is electrically equivalent to a photo-sensitive current source connected in parallel to a diode, figure 1.9 (Nelson, 2003). The short circuit photo-current ($J_{SC}$) is proportional to the intensity of the incident illumination. This photo-generated current is divided between a load resistance and a diode. The current flowing through the diode ($J_D(V)$) is a function of voltage across the device and flows in the opposite direction to $J_{SC}$. A rectifying diode has a non linear resistance, which produces an asymmetric current-voltage characteristic (Shockley, 1949; Sze and Ng, 2006). Equation 1.22 is the ideal diode equation:

$$J_0$$ is a constant, $e$ is electron charge, $V$ is the voltage across the device, $k$ is Boltzmann’s constant.
constant and $T$ is device temperature.

$$J_D(V) = J_0 \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right] \quad (1.22)$$

Current flowing through the diode generates a voltage, enabling charge separation. Without the asymmetry of the diode no voltage would be developed across the device. Sign convention defines $J_{SC}$ as the positive direction of current flow. The net flow of current ($J(V)$) is the product of photo and diode currents, equation 1.23.

$$J(V) = J_{SC} - J_D(V) \quad (1.23)$$

The current-voltage ($J-V$) characteristic of a solar cell is therefore defined by both the incident intensity of light and the diode characteristics, figure 1.10. A device operates on its characteristic at a position determined by the load resistance ($R_L$) between the two terminals of the solar cell. When $R_L = 0$ all the generated photo-current passes through the load and the device is effectively short circuited ($J(V) = J_{SC}$). No current passes through the diode and therefore no voltage is developed across the solar cell. As $R_L$ increases, current will start to flow through the diode reducing the current passing through the load and resulting in a voltage developing across the solar cell. In the case of $R_L = \infty$ no current will flow through the load and open circuit voltage $V_{OC}$ will be generated by the diode. Output electrical power ($P_{out}$) is the product of $J(V)$ and $V$. The optimal operating current ($J_{opt}$) and voltage ($V_{opt}$) is defined by maximum power point of the $J-V$ characteristic. A solar cell requires the
Figure 1.10: The Shockley ideal diode equation describes the current-voltage characteristics of a pn junction. Behaviour in the dark (solid line) and under illumination (dashed line) are both shown.

photo-sensitive current source to generate current and the diode to generate voltage. Both elements are therefore required to extract electrical power from a device. A pn junction is a semiconductor device which exhibits both necessary behaviours and is therefore the foundation of most real world PV devices.

1.6 Generation and recombination

Generation is the process of promoting an electron from the valence band into the conduction band generating a hole in the valence band. The reverse process, in which a conduction band electron relaxes into the valence band, is called recombination. In a semiconductor the energy required to excite an electron into the conduction band comes from three main sources: phonons, carriers and photons. During recombination, energy can be emitted via the same three interaction pathways. Phonon and carrier interactions are called non-radiative processes, whereas photon interactions are called radiative processes. Additional electronic states created by impurities and crystal defects can also act as generation and recombination centres.
1.6 Generation and recombination

Figure 1.11: The Fermi-Dirac distribution is temperature dependent. At 0 K the electron-hole population is described by a step function. With increasing temperature the distribution broadens allowing electrons to populate the conduction band and holes to population the valence band. $E_f$ is not temperature dependent. Black lines show density of states functions, red lines show Fermi-Dirac distributions and green lines show the density of carriers. Solid lines refer to electrons and dotted lines refer to holes.

### 1.6.1 Thermal generation and recombination

Thermal generation is the process of electron promotion via phonon interaction. Thermal energy in the lattice can be transferred to a valence band electron, exciting it into the conduction band, in a process called thermal generation. The reverse mechanism, in which electrons relax into lower energy states, returning energy to the lattice is called thermal recombination. Fermi-Dirac statistics (equation 1.14) describe the occupation of electronic energy levels as a function of temperature, figure 1.11. At absolute zero, $f_e(E, T, E_f)$ is a step function with no conduction band levels occupied. In this case the semiconductor will behave as a perfect insulator as it has no charge carriers. At room temperature, the Fermi-Dirac distribution will only permit a small free carrier population and as such most intrinsic semiconductors will be highly electrically resistive. An increase in free carrier population created by an increase in temperature will allow the material to behave like a conductor. Increasing temperature increases the rate of thermal generation of electrons. The rate of thermal recombination also increases, maintaining thermal and electrochemical equilibrium between the carrier population and the lattice.
1.6 Generation and recombination

The intrinsic carrier density \( n_i \) gives the density of thermally promoted electrons in the conduction band of a non-doped semiconductor, equation 1.24. This must equal the number of thermally generated valence band holes.

\[
n_i^2 = n_e(T, E_f)n_h(T, E_f) = N_e N_v \exp\left(\frac{-E_g}{kT}\right)
\]  

(1.24)

1.6.2 Radiative generation and recombination

A photon incident on a semiconductor with energy greater than \( E_g \) can promote an electron into the conduction band, generating a hole in the valence band. This process is called radiative generation. Conduction band electrons can release energy as a photon and return to the valence band, radiatively recombining with holes. Three radiative generation and recombination mechanisms must be considered in a semiconductor: stimulated absorption, stimulated emission and spontaneous emission. A two level model is used to illustrate these mechanisms in figure 1.12.

Both stimulated processes rely on incident photons and so the rate at which these occur is dependent on the incident spectrum. Stimulated absorption will occur relatively frequently under normal solar cell operating conditions because it can result from any photon with \( E > E_g \), and hence can be induced by a large component of the solar spectrum. The thermalisation of excited carriers means that emission processes are approximately monochromatic and therefore stimulated emission can only be achieved with an incident photon of energy \( \sim E_g \), which accounts for a very small component of the solar spectrum. Spontaneous emission is therefore the dominant radiative recombination mechanism.
1.6 Generation and recombination

Stimulated absorption

A photon with energy $E_2 - E_1$ is absorbed, promoting an electron from state 1 to state 2.

Stimulated emission

A photon with energy $E_2 - E_1$ stimulates an electron to relax from state 2 into state 1, releasing its energy as a photon of the same energy.

Spontaneous emission

An electron spontaneously relaxes from state 2 to state 1, releasing its energy as a photon of energy $E_2 - E_1$

$$f_{ph} f_1 (1 - f_2) \quad f_{ph} f_2 (1 - f_1) \quad f_2 (1 - f_1)$$

Figure 1.12: Mechanisms for radiative generation and recombination of electron-hole pairs with corresponding probabilities. $f_{ph}$ is the probability of a photon existing. $f_1$ is the probability that level 1 is occupied by an electron. $f_2$ is the probability that level 2 is occupied by an electron.

1.6.3 Carrier-carrier generation and recombination

Impact ionisation is a carrier-carrier scattering process which promotes an electron into the conduction band, figure 1.13a. In this process a high energy conduction band electron exchanges energy and momentum with a low energy valence band electron, producing two low energy conduction band electrons. The electron population does not acquire any additional energy despite an extra electron being promoted into the conduction band. This process occurs with a very low probability because it requires a high energy conduction band electron which is unlikely to exist as a result of thermal generation. The reverse process is called Auger recombination, figure 1.13b, here two low energy conduction band electrons interact. One electron recombines with a valence band hole, transferring energy and momentum to the other electron, exciting it high into the conduction band. Following Auger recombination the remaining high energy conduction band electron will experience rapid thermalisation, returning it to the conduction band edge, and as such, energy is lost from the carrier population as heat. The probability with which carrier-carrier interaction mechanisms occur is dependent on carrier density. Auger processes can become a significant source of loss in highly doped...
1.6 Generation and recombination

(a)

Figure 1.13: a) Impact ionisation and b) Auger recombination are carrier-carrier generation and recombination mechanisms respectively. Electrons before interaction (white dots) and electrons after interaction (black dots) are shown along with thermalisation steps (red lines).

(b)

Materials or at high temperature. Carrier-carrier processes have a greater effect in indirect bandgap semiconductors, such as silicon, where radiative mechanisms are suppressed.

1.6.4 Impurity and surface generation and recombination

In real world solar cells the semiconductor lattice cannot be produced perfectly uniformly without defects. Impurities are unavoidably introduced to the structure during crystal growth. The crystal lattice of a real world device will not be infinite in extent and additional impurities and broken bonds are concentrated at surfaces and material interfaces. These impurities and defects can create additional electronic states in the forbidden energy region of the semiconductor. Carriers can access these states via phonon or photon interaction, although phonon interaction occurs at a much faster rate and therefore impurity and surface generation and recombination mechanisms are generally considered to be non-radiative processes.

Impurity and defect states act as carrier traps. They are bound in the crystal structure and so have a fixed location. Any free carrier caught in this state is then also fixed in location until either it can be released thermally or a carrier of the opposite polarity is captured into the
1.7 Thermal energy into chemical potential energy

same state, forcing recombination. Trap states reduce device efficiency in two ways: acting as recombination centres and impeding carrier transport.

In the absence of any radiative generation, trap state generation and recombination are equal. The rate at which electrons are captured in impurity states is dependent on the density of electrons in the conduction band and the density of holes in the impurity states. The rate of generation however only depends on the density of electrons in the impurity states. Under illumination the electron density of the conduction band increases and trap state recombination mechanisms occur at a faster rate than the competing generation processes. Recombination occurring via impurity states is often referred to as Shockley Read Hall recombination (Shockley and Read, 1952) and in many real world devices this is the dominant recombination mechanism.

1.7 Thermal energy into chemical potential energy

Instantaneously after stimulated absorption occurs, carriers have an energy distribution which is described by that of the incident spectrum. Excited carriers rapidly interact with lattice phonons and the carrier populations cool to the band edges, as they form distributions with the minimum free energy. For most realistic PV operating conditions, thermalisation occurs at a much faster rate than any band-to-band transition hence, under constant illumination, the excited carriers form steady state populations in thermal equilibrium with the lattice. The shape of the Fermi-Dirac distribution is determined by the temperature of the carrier population. The value of the Fermi level is described by the steady state carrier density. In a solar cell under constant illumination, electron and hole populations are described by a Fermi-Dirac distribution at room temperature, although the two distributions have separate Fermi levels (Würfel, 1995).

The density of the electron and hole populations is determined by the relative rates of the generation and recombination processes. Under solar illumination, the rate of generation exceeds that of recombination and net generation occurs. This results in an increase in electron density in the conduction band, which causes the Fermi level describing the electron
1.7 Thermal energy into chemical potential energy

Figure 1.14: A pn junction under illumination is no longer in chemical equilibrium. $V_{bi}$ draws photo-excited carriers to their respective terminals causing a splitting of electron and hole quasi-Fermi levels. Chemical potential, proportional to incident photon flux, develops across the device.

Population ($E_{fc}$) to shift towards the conduction band edge. A corresponding increase in the hole density in the valence band causes the Fermi level describing the hole population ($E_{fv}$) to shift towards the valence band edge. The separation between $E_{fc}$ and $E_{fv}$ is the chemical potential ($\mu$) generated in the device per electron-hole pair, equation 1.25.

$$\mu = E_{fc} - E_{fv} = eV$$  \hspace{1cm} (1.25)

The chemical potential describes the entropy free energy which can be extracted as useful electrical work and that an electron-hole pair can deliver to a load (Würfel, 1982), figure 1.14. Chemical potential is given by the product of electron charge ($e$) and the voltage ($V$) across the device. Illuminating a semiconductor is often referred to as optical biasing. The increase in carrier density which derives from net generation in a device will also result in an increase in spontaneous emission and trap state recombination as the density of the excited state carrier population increases. When no current is extracted (open circuit) and the rate of stimulated absorption is equal to the sum of spontaneous emission and trap state recombination, a steady state carrier population will be established under constant illumination.

An expression for device open circuit voltage, as a function of absorbed photons ($n_{ph}(E > E_g)$), can be derived from the carrier population densities. The total number of conduction band electrons and valence band holes in a device under illumination is given by equations 1.26 and 1.27. The expressions are analogous to equations 1.18 and 1.20 but allow electron and hole
Fermi levels to take separate values.

\[ n_e(T, E_{fc}) = N_c \exp\left(-\frac{E_c - E_{fc}}{kT}\right) \]  \hspace{1cm} (1.26)

\[ n_h(T, E_{fv}) = N_v \exp\left(-\frac{E_{fv} - E_v}{kT}\right) \]  \hspace{1cm} (1.27)

The product of \( n_e(T, E_{fc}) \) and \( n_h(T, E_{fv}) \) is a function of \( \mu \), equation 1.28.

\[ n_e(T, E_{fc})n_h(T, E_{fv}) = N_cN_v \exp\left(-\frac{E_g}{kT}\right) \exp\left(\frac{E_{fc} - E_{fv}}{kT}\right) \]

\[ = n_i^2 \exp\left(\frac{\mu}{kT}\right) \]  \hspace{1cm} (1.28)

The sum of absorbed photons (\( n_{ph}(E > E_g) \)) and thermally generated pairs (\( n_i \)) all squared, is given by the product of electron number and hole number, equation 1.29.

\[ (n_{ph}(E > E_g) + n_i)^2 = n_e(T, E_{fc})n_h(T, E_{fv}) \]  \hspace{1cm} (1.29)

Substituting this expression into equation 1.28 provides equation 1.30. This relationship is illustrated in figure 1.15.

\[ \epsilon V_{OC} = 2kT \ln\left(\frac{n_{ph}(E > E_g) + n_i}{n_i}\right) \]  \hspace{1cm} (1.30)

### 1.7.1 Current extraction

When a finite load resistance is placed across the terminals of an illuminated solar cell some current will flow. As carriers are extracted the density of the steady state carrier populations is reduced and hence the associated chemical potential is also reduced. For zero load resistance the device is operating at short circuit and all photo-generated carriers are extracted. Under this condition the steady state carrier density is the same as for a device in the dark and hence the chemical potential of the electron and hole populations is zero. Figure 1.16 shows
Solar energy can be directly converted into useful electrical work in a photovoltaic device. Such a conversion will only occur in a device exhibiting two essential features: photo-sensitive current generation and asymmetric electrical resistance.

The Sun behaves as a black body emitting photons over a broad spectrum of energies. An efficient solar cell should be well matched to the solar spectrum and so must be able to absorb a broad range of energies. This requires a material with electronic energy levels that provide a continuum of energy transitions. A continuum of electronic energy transitions can also act as a staircase which excited electrons will rapidly descend, in search of thermal equilibrium. The thermalisation of excited carriers can be interrupted by a break in the available electronic transitions. A semiconductor has a continuum of electronic energy levels broken up by a forbidden energy region called a bandgap ($E_g$). This acts to interrupt thermalisation however,
it also limits the range of photon energies which will be absorbed. Only photons with energies greater than $E_g$ will be absorbed in the device.

In a semiconductor, the band of energy levels below $E_g$ is called the valence band and the band of energies above $E_g$ is called in conduction band. Electrons excited into the conduction band are free to move in the semiconductor and act as current carriers. A pn junction is a semiconductor device made from two layers of oppositely doped material. This device has a built-in voltage across it, which draws charge carriers to their respective terminals. A pn junction provides resistive asymmetry, which is necessary to deliver carriers to an electrical circuit.

Generation in a solar cell is the process of electron promotion from the valence band into the conduction, leaving a positively charged electron vacancy (a hole) in the valence band. Recombination describes an electron returning to the valence band, and occupying a vacancy. These processes require the conservation of energy and momentum. Interaction particles, which supply or dissipate energy and momentum, are required for generation or recombination to occur. Photons, thermal lattice vibrations (phonons) and other carriers can all act as interaction particles. The absorption of a photon is a generation process in which a photon
supplies the necessary energy to promote an electron into the conduction band.

Under illumination, the carrier density in a solar cell increases. Thermalisation occurs at a much faster rate than band-to-band processes and therefore, under constant illumination, the steady state carrier population is in thermal equilibrium with the surrounding lattice. After thermalisation, electron and hole populations cease to be in chemical equilibrium and the two populations are separated by a chemical potential. This chemical potential describes the free electrical work each electron-hole pair can perform on a load and is the product of electronic charge and voltage. When the two terminals of a solar cell are connected by a finite load some current will flow. This reduces the density of the carrier population, which in turn reduces the chemical potential across the device. Current and voltage in a solar cell therefore have an inverse relationship.
Fundamental limiting efficiency

The conversion of solar radiation into useful electrical work can never be 100% efficient. Fundamental limiting efficiency has been discussed by many authors with several analyses being presented. Shockley and Queisser published a detailed balance approach, using the generalised Planck formalism to identify current-voltage characteristics, with the maximum power point giving the fundamental limiting efficiency (Araújo and Martí, 1994; Shockley and Queisser, 1961). Other authors have derived consistent results from a thermodynamic approach. By considering energy and entropy fluxes, limits to photovoltaic conversion are established (Vos et al., 1993; Würfel, 2002). In this chapter five intrinsic loss processes are quantified. These processes account for all incident solar radiation and lead to fundamental limiting efficiency. An analytical approach is taken to highlight physical mechanisms, obscured in previous numerical studies. It is found that the free energy available per carrier is limited by a Carnot factor resulting from the conversion of thermal energy into entropy free work, a Boltzmann factor arising from the mismatch between absorption and emission angles and
also carrier thermalisation. It is shown that in a degenerate band absorber a free energy advantage is achieved over a discrete energy level absorber due to entropy transfer during carrier cooling. The non-absorption of photons with energy below the bandgap and photon emission from the device are shown to be current limiting processes. All losses are evaluated using the same approach providing a complete mathematical and graphical description of intrinsic mechanisms leading to limiting efficiency. Intrinsic losses in concentrator cells and spectrum splitting devices are considered and it is shown that dominant intrinsic losses are theoretically avoidable with novel device designs.

2.1 Generalised Planck equation

The generalised Planck equation is an adaptation of Planck’s law of radiation, which can be used to describe photon emission from a carrier population with chemical potential. The emitted photon population is in thermal and chemical equilibrium with the steady state electron and hole populations and therefore also has a chemical potential associated with it. The photon flux \( n_{ph}(E, T, \mu, \Omega) \) emitted from a black or grey body per unit energy interval is the product of available photon states, the probability of their occupation, and the emissivity of the material, \( \epsilon(E) \). This expression is called the generalised Planck equation, equation 2.1, and is derived in Appendix A.

\[
n_{ph}(E, T, \mu, \Omega) = \epsilon(E) \frac{2 \Omega}{c^2 h^3} \frac{E^2}{\exp[(E - \mu)/kT] - 1} \quad (2.1)
\]

The generalised Planck equation can be used to describe the Sun’s emission using \( \epsilon(E) = 1 \), \( \mu = 0 \), and \( \Omega = 6.8 \times 10^{-5} \), corresponding to equation 1.1. In the case of emission from a solar cell \( \epsilon(E) \) can be approximately described by a step function with the emission threshold at \( E_g \), \( \mu = eV \) and emission is over a hemisphere giving \( \Omega = \pi \).
2.2 Detailed balance

Detailed balance is a principle of statistical mechanics which requires a process to occur at the same rate as the reverse process when a system is in equilibrium. This basis provides a method of calculating current-voltage characteristics for a device by balancing the relative rates of absorption and emission. In a steady state, the difference between the number of photons absorbed by the device and the number of photons emitted gives the photo-generated current, assuming no trap state recombination occurs. The method can be evaluated with real spectral data to describe the $J - V$ characteristic of a real world device. Alternatively, the generalised Planck equation can be used to determine absorption and emission currents, allowing ultimate solar conversion limits of idealised devices to be calculated.

2.2.1 Shockley Queisser limiting efficiency

The Shockley Queisser limiting efficiency is derived using a detailed balance, generalised Planck formalism, and is the ultimate conversion efficiency achievable in a single junction device, under one Sun illumination (Shockley and Queisser, 1961). The difference between the number of photons absorbed by the device, $n_{ph}(E, T_S, \mu = 0, \Omega_S)$, and the number of photons emitted, $n_{ph}(E, T_L, \mu, \Omega_C)$, integrated over all photon energies, gives the number of carriers contributing to the photo-generated current, equation 2.2. Multiplying by the electronic charge converts carrier number into current.

$$J = e \int_{0}^{\infty} [n_{ph}(E, T_S, \mu = 0, \Omega_S) - n_{ph}(E, T_L, \mu, \Omega_C)] \, dE$$

$$= e \int_{0}^{\infty} \left[ a(E) \left( \frac{2\Omega_S}{c^2 h^3} \right) \frac{E^2}{\exp[E/kT_S] - 1} - \epsilon(E) \left( \frac{2\Omega_C}{c^2 h^3} \right) \frac{E^2}{\exp[(E - \mu)/kT_L] - 1} \right] \, dE$$

$a(E)$ and $\epsilon(E)$ can be approximated as a step function, equation 2.3. This is incorporated into equation 2.2 by changing the lower limit of integration to $E_g$, as shown in equation 2.4.

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

(2.3)
\[ J = e \int_{E_g}^{\infty} \left[ \left( \frac{2\Omega_S}{\hbar^3} \right) \frac{E^2}{\exp[E/kT_s] - 1} - \left( \frac{2\Omega_C}{\hbar^3} \right) \frac{E^2}{\exp[(E - \mu)/kT_L] - 1} \right] dE \] (2.4)

Electrical power which can be extracted from the device is the product of current and voltage and the efficiency of the device is determined by dividing output power by the total power in the incident solar spectrum (\( P_{in} \)) (equation 2.5).

\[ \eta = \frac{JV}{P_{in}} \] (2.5)

Figure 2.1 shows \( J-V \) characteristics for idealised devices with a range of \( E_g \). The power efficiency of each device is also shown. \( E_g = 1.31eV \) provides the maximum device efficiency of 31%, at the optimal operating voltage. Devices with a lower \( E_g \) absorb more of the solar spectrum and hence have a larger \( J_{SC} \) however, more energy is dissipated in the lattice as heat giving lower \( V_{OC} \). Devices with a higher \( E_g \) have a lower \( J_{SC} \) as more of the solar spectrum is transmitted however, it will have a higher \( V_{OC} \) because excited carriers retain more of their energy.

### 2.2.1.1 Shockley Queisser assumptions

Several assumptions have been made in deriving the Shockley Queisser limit:

1. The solar cell has a step like absorption and emission profile and 100% of incident photons with energy above \( E_g \) are absorbed. This would only occur in an infinitely thick device because light incident on an absorber is attenuated exponentially with penetration depth.

2. Each incident photon produces a single electron-hole pair. No impact ionisation or Auger recombination occurs in the device. This is a reasonable assumption for many real world devices. However, Auger recombination can be a significant loss mechanism in indirect bandgap materials such as silicon.

3. The crystal is perfect and infinite, with no trap states and therefore no impurity or surface recombination.
2.3 Intrinsic loss mechanisms in solar cells

Loss processes occurring in a single bandgap device under one Sun illumination can be divided into two distinct categories. Extrinsic losses such as series resistance, parasitic recombination and contact shadowing can substantially limit device efficiency however, they are theoretically avoidable and consequently are not considered when calculating fundamental limiting efficiency. Intrinsic losses are unavoidable in this device design and will still be present in an idealised solar cell (Henry, 1980).

2.3.1 Qualitative description of intrinsic losses

2.3.1.1 Below $E_g$ loss

Only photons with energy above the bandgap of the semiconductor will have sufficient energy to generate an electron-hole pair. In this idealised model all photons with sufficient energy
2.3 Intrinsic loss mechanisms in solar cells

will be absorbed and other photons are transmitted and will not contribute to the useful power output. Below $E_g$ loss derives from the spectral mismatch between the broad solar spectrum and the single threshold absorption of a semiconductor device. This loss mechanism reduces the number of incident photons able to induce stimulated absorption. The first term in equation 2.4 describes stimulated absorption in the device. In a higher bandgap material the range of integration will be reduced as will the available current.

2.3.1.2 Emission loss

Spontaneous emission in a solar cell is described by the second term in equation 2.4. This emission is a function of the device temperature and the voltage across the device. The radiative recombination of carriers competes with stimulated absorption and therefore reduces the available current. In a device under one Sun illumination, at room temperature, emission loss is approximately zero in a device under short circuit conditions. As load resistance increases and the device moves towards optimal operating voltage emission loss increases.

2.3.1.3 Thermalisation loss

Similarly to below $E_g$ loss, thermalisation loss derives from the spectral mismatch between the solar spectrum and the semiconductor absorption profile. Following photo-generation, excited carriers rapidly interact with lattice phonons, losing energy as heat to the surroundings. Thermalisation occurs at a much faster rate than any radiative process in the solar cell and therefore, under constant illumination, steady state electron and hole populations are in thermal equilibrium with the lattice. Effectively all photon energy above the bandgap of the material is lost as heat. Thermalisation loss reduces the free energy available per carrier and therefore is a voltage loss mechanism. It is the dominant loss mechanism in many real world devices. Without thermalisation carriers would remain hot and the device would behave much like a solar thermal heat engine, with heat energy, rather than chemical energy driving a load.
2.3 Intrinsic loss mechanisms in solar cells

2.3.1.4 Carnot loss

Once carriers are fully thermalised with the lattice they have energy equal to the bandgap of the semiconductor however, the free energy per carrier which can be extracted as useful work is lower. The free energy is described by the chemical potential of the carrier populations. Carnot’s equation describes the work which can be extracted when energy is transferred from a hot source (the Sun) to a cold sink (the atmosphere). As the carrier population cools, thermal energy is transferred into entropy free chemical energy, which can be extracted as useful electrical work. In a lattice at 0 K all thermal energy will be transferred in this way however, real world cells will have a finite temperature and therefore not all thermal energy can be converted. The reduction in free energy available per carrier as a result of incomplete thermalisation is described by the Carnot factor. In a colder lattice, more thermal energy is transferred into chemical energy, making colder devices fundamentally more efficient solar converters.

2.3.1.5 Boltzmann loss

Boltzmann loss derives from the mismatch between the solid angle of absorption ($\Omega_S$) and the solid angle of emission ($\Omega_C$). Photons are absorbed through the solid angle subtended by the solar disk, $\Omega_S = 6.8 \times 10^{-5}$ sr. By contrast, emission from the cell is over a hemisphere, $\Omega_C = \pi$ sr, figure 2.2. This irreversible expansion of photon modes generates entropy, further reducing the free energy available per carrier. This mismatch means that there are more photon states allowing spontaneous emission than those allowing stimulated absorption. Under constant illumination carriers will form a steady state population in thermal equilibrium with the lattice. The number of carriers in this population is determined by the relative rates of photo-generation, current extraction and photo-recombination. The solid angle mismatch favours recombination, reducing the carrier population and therefore reducing the quasi-Fermi level splitting and the resulting carrier chemical potential. Lenses and mirrors can be used to focus the light onto the solar cell, expanding the solid angle of absorption. This increases the number of photon states available for stimulated absorption. Equally, novel cell structuring
Figure 2.2: Solar radiation described by $T_S = 6000$ K and $\mu = 0$ eV (wavy lines) is absorbed in a solar cell through solid angle $\Omega_S = 6.8 \times 10^{-5}$ sr. Emission from the cell is over a hemisphere ($\Omega_C = \pi$ sr) and is characterised by $T_L = 300$ K and $\mu = \epsilon V_{opt}$ (dashed lines).
or sophisticated cell coatings can be used to restrict the angle of emission, reducing the recombination rate. Both methods have the effect of enabling a larger steady state carrier population, increasing the free energy available per carrier.

2.3 Intrinsic loss mechanisms in solar cells

2.3.2 Quantitative description of intrinsic losses

The generalised Planck, detailed balance formalism has been used here to quantify intrinsic loss mechanisms.

2.3.2.1 Deriving the optimal operating voltage analytically

As can be seen from equations 2.4 and 2.5, efficiency is described by two independent variables: $E_g$ and $V$, therefore the maximum achievable efficiency is calculated by evaluating two partial differential equations (equations 2.6 and 2.7).

$$
\left( \frac{\partial \eta}{\partial E_g} \right)_V = 0 \tag{2.6}
$$

$$
\left( \frac{\partial \eta}{\partial V} \right)_{E_g} = 0 \tag{2.7}
$$

An analytical solution to equation 2.6 is found by taking the Boltzmann approximation, neglecting the $-1$ in the denominator of the generalised Planck equation. This solution provides a relationship between the optimal operating voltage ($V_{\text{opt}}$) and $E_g$ (equation 2.8).

$$
V_{\text{opt}} = E_g \left( 1 - \frac{T_L}{T_S} \right) - T_L k \ln \left( \frac{\Omega_C}{\Omega_S} \right) \tag{2.8}
$$

The first term in equation 2.8 is the Carnot factor previously derived in this manner by Landsberg and Badescu (Landsberg and Badescu, 2000). The second term is referred to here as the Boltzmann factor because it takes the form of Boltzmann’s equation representing entropy generation with increased occupancy of available states, $\Delta S = k \ln (\Omega_C/\Omega_S)$. The
2.3 Intrinsic loss mechanisms in solar cells

Figure 2.3: An approximate analytical solution for $V_{opt}/E_g$ is compared to an exact numerical calculation for a cell under maximum concentration. The two equate at the optimal bandgap for this concentration.

energy flow associated with that entropy generation is given by $T\Delta S$. Markvart’s study of the thermodynamics of optical étendue derives this term from a different basis (Markvart, 2008). The relation shown in equation 2.8 shows that the useful work available per carrier is limited by unavoidable heat loss to the surroundings (Carnot factor) and irreversible entropy generation (Boltzmann factor).

2.3.2.2 Justifying approximations

**Optimal voltage approximation** Under maximum concentration ($\Omega_C = \Omega_S$) the Boltzmann factor tends to zero. Under this condition the value of $V_{opt}$ will be exact for a device with optimal bandgap, when the condition in equation 2.7 is also satisfied. Away from this value $V_{opt}$ is only approximate. The accuracy of this approximation is shown in figure 2.3 where the approximate analytical solution for $V_{opt}/E_g$ is plotted alongside an exact numerical calculation for a cell under maximum concentration. The two equate at the optimal bandgap for this concentration. Analytically calculated $V_{opt}$ is lower than the numerical calculation for devices with $E_g$ below the optimal, and higher for devices with $E_g$ above the optimal. Within 0.1 eV of the optimal bandgap analytical and numerical solutions differ by $<0.004$ eV.
2.3 Intrinsic loss mechanisms in solar cells

Figure 2.4: a) The ratio of $V_{OC}$ (calculated analytically) to $V_{OC}$ (calculated numerically) is shown as a function of $E_g$. b) The ratio of $J_{SC}$ (calculated analytically) to $J_{SC}$ (calculated numerically) is shown as a function of $E_g$.

**Boltzmann approximation** At low energies the effect of the -1 in the denominator of the generalised Planck (equation 2.1) becomes significant and the Boltzmann approximation is no longer valid. In the regime of realistic bandgaps ($E_g > 0.5$ eV) taking the Boltzmann approximation has a negligible effect on the calculation of $V_{opt}$ (figure 2.4a). The Boltzmann approximation has a more significant effect on current calculation (figure 2.4b). Total incident photon flux calculated with the approximation is 83% of that calculated without. Absorbed photon flux is calculated in the same way and so will be lower than its true value for low $E_g$ devices however, with increasing $E_g$, analytical values for absorbed photon flux tend to their numerical values. Device efficiency is a function of the ratio of absorbed photon flux to total incident photon flux and as such inaccuracies in current calculation, deriving from the Boltzmann approximation, cancel out for low $E_g$ devices. With increasing $E_g$, cancellation does not take place and so device efficiencies appear slightly higher than their numerical counterparts.

The net effect of these approximations is for analytically calculated efficiencies to appear slightly lower than their numerically calculated values for low $E_g$ devices and slightly higher for high $E_g$ devices.
2.3 Intrinsic loss mechanisms in solar cells

2.3.2.3 Current-Voltage characteristics

All loss processes result in either a reduction in current or a reduction in voltage. Below $E_g$ and emission losses limit the number of available carriers and these are therefore current reduction process. Thermalisation, Boltzmann and Carnot losses all reduce the energy with which carriers can be extracted and therefore are voltage drop processes. Reductions in current and voltage due to intrinsic losses are shown in figure 2.5 for a device under one Sun illumination. The total area gives the power in the incident solar spectrum. The areas of the different shaded regions give the power attributed to the different intrinsic loss processes. Once all current and voltage drop processes are accounted for the current-voltage characteristic of the device is derived.

2.3.2.4 Accounting for all the Sun’s energy

An analytical approach has been used to quantify all intrinsic losses and to calculate power out (Table 2.1).

$$
\chi(E, T) = \frac{2kT}{e^2h^3} (E^3 + 3E^2kT + 6Ek^2T^2 + 6k^3T^3)
$$

(2.9)

$$
\gamma(E, T) = \frac{2kT}{c^2h^3} (E^2 + 2kTE + 2k^2T^2)
$$

(2.10)

$$
J_{opt} = \int_{E_g}^{\infty} n(E, T_S, 0, \Omega_S) dE - \int_{E_g}^{\infty} n(E, T_L, eV_{opt}, \Omega_C) dE
$$

$$
\approx \Omega_S \gamma(E_g, T_S) \exp\left(\frac{-E_g}{kT_S}\right) - \Omega_C \gamma(E_g, T_L) \exp\left(\frac{eV_{opt} - E_g}{kT_L}\right)
$$

substitute equation 2.8

$$
\approx \Omega_S \left[ \gamma(E_g, T_S) \exp\left(\frac{-E_g}{kT_S}\right) - \gamma(E_g, T_L) \exp\left(\frac{-E_g}{kT_S}\right) \right]
$$

(2.11)
2.3 Intrinsic loss mechanisms in solar cells

Figure 2.5: Intrinsic loss mechanisms are shown for a Shockley Queisser solar cell with $E_g = 1.31$ eV, under one Sun illumination. The outer curve is given by the number of incident solar photons with energy $\geq$ the x-axis value hence, the total area of the shaded region describes the power of the incident solar spectrum. The power sacrificed to different intrinsic loss mechanisms is given by the areas of the different shaded regions. Photon number (y-axis) is multiplied by electron charge and energy (x-axis) is expressed in units of (eV) to allow a J-V curve for this idealised device to be superimposed on the plot. Intrinsic loss mechanisms can then be defined as either current limiting or voltage limiting. This plot shows that emission loss and below $E_g$ loss both reduce $J_{opt}$, whereas Carnot loss, Boltzmann loss and thermalisation loss all reduce $V_{opt}$. Changing $E_g$ moves the $J_{SC}$-$V_{OC}$ point along the outer curve changing the relative significance of the different intrinsic loss mechanisms (Hirst and Ekins-Daukes, 2011).
### 2.3 Intrinsic loss mechanisms in solar cells

Below $E_g$

\[
\int_0^{E_g} E \cdot n(E, T_S, 0, \Omega_S) \, dE \\
\approx \Omega_S \left( \chi(0, T_S) - \exp \left( -\frac{E_g}{kT_S} \right) \chi(E_g, T_S) \right)
\]

**Thermalisation loss**

\[
\int_{E_g}^{\infty} E \cdot n(E, T_S, 0, \Omega_S) \, dE - E_g \int_{E_g}^{\infty} n(E, T_S, 0, \Omega_S) \, dE
\]

\[
\approx \Omega_S \exp \left( -\frac{E_g}{kT_S} \right) \left( \chi(E_g, T_S) - E_g \cdot \gamma(E_g, T_S) \right)
\]

**Emission loss**

\[
E_g \int_{E_g}^{\infty} n(E, T_L, eV_{opt}, \Omega_C) \, dE
\]

\[
\approx \Omega_C E_g \gamma(E_g, T_L) \exp \left( \frac{eV_{opt} - E_g}{kT_L} \right)
\]

substitute equation 2.8

\[
\approx \Omega_S E_g \gamma(E_g, T_L) \exp \left( -\frac{E_g}{kT_S} \right)
\]

**Boltzmann loss**

\[
kT_L \ln \left( \frac{\Omega_C}{\Omega_S} \right) J_{opt}
\]

**Carnot loss**

\[
E_g \left( \frac{T_L}{T_S} \right) J_{opt}
\]

**Power out**

\[
J_{opt} V_{opt}
\]

| Table 2.1: | All mechanisms are analytically described. $\chi(E, T)$, $\gamma(E, T)$ and $J_{opt}$ are represented in equations 2.9, 2.10 and 2.11 respectively. |
2.3 Intrinsic loss mechanisms in solar cells

<table>
<thead>
<tr>
<th>mechanism</th>
<th>efficiency at ( E_g = 1.31 \text{ eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>power out</td>
<td>0.325</td>
</tr>
<tr>
<td>below ( E_g ) loss</td>
<td>0.250</td>
</tr>
<tr>
<td>thermalisation loss</td>
<td>0.298</td>
</tr>
<tr>
<td>Carnot loss</td>
<td>0.022</td>
</tr>
<tr>
<td>Boltzmann loss</td>
<td>0.093</td>
</tr>
<tr>
<td>emission loss</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Table 2.2: The fraction of incident solar energy attributed to different mechanisms for a device under one Sun illumination with \( E_g = 1.31 \text{ eV} \). It should be noted that maximum power out occurs at \( E_g = 1.35 \text{ eV} \) in this analytical model however, values at 1.31eV are shown to allow comparison with numerical models.

In order to calculate the fraction of incident solar radiation a loss process consumes or to calculate device efficiency, equations in table 2.1 should be divided by total incident solar energy current \( P_{\text{in}} \) (equation 2.12).

\[
P_{\text{in}} = \int_0^{\infty} E \cdot n(E, T_S, 0, \Omega_S) \, dE \\
\approx \Omega_S \chi(0, T_S) \quad (2.12)
\]

All incident solar radiation is accounted for so that the mechanisms leading to limiting efficiency are fully described. Losses and power out are plotted with varying \( E_g \) in figure 2.6. It should be noted that these results are approximate. Away from the optimal bandgap the value of \( V_{\text{opt}} \) used is not exact as shown in figure 2.3. In addition, the Boltzmann approximation has been taken to enable an analytical solution. Device efficiencies calculated with and without Boltzmann approximations in the region \( 0.5 \text{ eV} < E_g < 3.5 \text{ eV} \) differ by a maximum of 1.9%.

In figure 6 a numerical solution for power out is shown alongside the analytical solution to show that the combined effect of these approximations is small.

The device efficiency shown in table 2.2 is comparable to the device efficiency calculated analytically by Shockley and Queisser (Shockley and Queisser, 1961), 0.31 at \( E_g = 1.31 \text{ eV} \). Thermalisation and below \( E_g \) are the dominant loss processes (table 2.2). Thermalisation loss reduces with increasing bandgap while below \( E_g \) loss increases. This is because increasing
2.3 Intrinsic loss mechanisms in solar cells

Figure 2.6: Intrinsic loss processes and hence, power out are shown to be dependent on $E_g$. All incident radiation is accounted for illustrating why intrinsic loss mechanisms lead to fundamental limiting efficiency.
the bandgap reduces the number of absorbed photons while increasing the energy with which they can be extracted. Boltzmann loss is also a substantial loss mechanism, resulting in a 9.3% efficiency reduction at $E_g = 1.31$ eV.

### 2.3.3 Comparing discrete and degenerate absorbers

By deriving open circuit voltage ($V_{OC}$) analytically from the generalised Planck detailed balance formalism it is shown that the degenerate semiconductor energy bands have an inherent entropic advantage over discrete absorbers such as molecular systems.

Under the conditions of open circuit voltage ($V_{OC}$) no current flows. $V_{OC}$ can therefore can be derived substituting $J = 0$ into equation 2.4. Taking the Boltzmann approximation and integrating by parts gives equation 2.13.

$$\exp \left\{ \frac{eV_{OC}}{kT_L} \right\} = \frac{\Omega_C}{\Omega_S} \frac{\gamma(E_g, T_S)}{\gamma(E_g, T_L)} \exp \left\{ \frac{E_g}{kT_L} \left( 1 - \frac{T_L}{T_S} \right) \right\}$$

Which yields,

$$V_{OC} = E_g \left( 1 - \frac{T_L}{T_S} \right) - kT_L \ln \left( \frac{\Omega_C}{\Omega_S} \right) + kT_L \ln \left( \frac{\gamma(E_g, T_S)}{\gamma(E_g, T_L)} \right)$$

The first and second terms of equation 2.14 are the Carnot and Boltzmann factors respectively. The third term describes an increase in the free energy per carrier. This occurs as a result of the mismatch between the temperatures of the absorbed and emitted photon distributions (Markvart, 2008). The strong interaction between excited carriers and lattice phonons results in heat transferring from the carrier distribution to the lattice. Entropy is also transferred to the lattice in this cooling process, decreasing the entropy of the excited carrier population. The total entropy of the electron population and the lattice combined still increases, in accordance with the second law of thermodynamics. The free energy available in the carrier distribution can be described by Helmholtz free energy (equation 2.15), where $H$ is the Helmholtz free.
2.3 Intrinsic loss mechanisms in solar cells

energy of the carrier distribution, $U$ is the internal energy of the carrier distribution, $T$ is the temperature of the carrier distribution and $S$ is the entropy of the carrier distribution.

$$H = U - TS \quad (2.15)$$

The cooling of carriers reduces $U$ however, some of this loss is recouped because the corresponding reduction in $T$ and $S$ results in the slight increase in free energy available per carrier described in the third term of equation 2.14. The degenerate nature of absorption bands enables this free energy advantage and as such, the free energy available per carrier in a discrete energy level absorber is lower.

In a two level discrete absorber, carrier cooling does not occur because in an infinitely narrow absorption band all carriers are absorbed and emitted with the same energy (monochromatic light). The increase in available free energy per carrier as a result of cooling described in the third term of equation 2.14 is zero for a discrete absorber. Equation 2.16 describes current flow in a device with two energy levels of finite width $\Delta E$, separated by $E_{12}$, figure 2.7. In the limit $\Delta E \rightarrow 0$ equation 2.16 can be evaluated analytically as shown in equation 2.17.

$$J_{E_{12}} = \int_{E_{12}}^{E_{12} + 2\Delta E} n(E, T_S, 0, \Omega_S) \, dE - \int_{E_{12}}^{E_{12} + 2\Delta E} n(E, T_L, \mu, \Omega_C) \, dE \quad (2.16)$$
2.4 Implications for solar cell design

Figure 2.8: Normalised I-V curves for discrete and degenerate absorbers with $E_{12} = E_g = 1.31$ eV under one Sun illumination. $V_{OC}$ is higher for the degenerate absorber because of the entropy transfer occurring as a result of carrier cooling.

$$J_{E_{12}} = \frac{2E_{12}^2}{e^2 h^3} \left( \Omega_S \exp \left( \frac{-E_{12}}{kT_S} \right) - \Omega_C \exp \left( \frac{eV - E_{12}}{kT_L} \right) \right) \Delta E \quad (2.17)$$

Taking $J_{E_{12}} = 0$ yields,

$$V_{OC} = E_{12} \left( 1 - \frac{T_L}{T_S} \right) - kT_L \ln \left( \frac{\Omega_C}{\Omega_S} \right) \quad (2.18)$$

Comparing equations 2.14 and 2.18 shows that the free energy per carrier is greater in a degenerate system because carrier cooling results in entropy transfer away from the carrier distribution, figure 2.8.

2.4 Implications for solar cell design

While the Shockley Queisser limiting efficiency is the fundamental limit for solar conversion in a single junction device under one Sun illumination, it is far from the ultimate limit for any method of solar conversion. Devices can be designed to exceed the Shockley Queisser limit by accessing the five intrinsic loss mechanisms. Solar cells exceeding this limit are often referred to as third generation devices (Green, 2006). These devices are designed to access
the dominant intrinsic loss mechanisms which lead to Shockley Queisser limiting efficiency.
Thermalisation loss, below $E_g$ loss and Boltzmann loss account for 30%, 25% and 10% of the incident solar spectrum respectively. Substantial efficiency benefits can only come from targeting these loss mechanisms.

A simple design enhancement is to concentrate incident solar radiation onto a solar cell using lenses or mirrors. This reduces the voltage drop associated with the Boltzmann loss, increasing efficiency. The same effect can be achieved in a device with restricted angular emission. Figure 2.9 shows how the fraction of solar energy which can be extracted as useful work varies with concentration for fixed $E_g$. With 215 times solar concentration the fraction of incident solar energy lost because of absorption and emission angle mismatch is half that at one Sun. The fraction of incident solar radiation lost via other intrinsic loss processes is independent of absorption and emission angles as can be seen by dividing the equations in table 2.1 by equation 2.12.

In a hot carrier solar cell interactions between excited electrons and lattice phonons are impeded and the electron population temperature remains higher than that of the lattice (Würfel, 1997). In an idealised hot carrier solar cell discrete energy selective contacts extract these hot carriers eliminating thermalisation loss.

Substantial efficiency advantages can be achieved by splitting the broad solar spectrum into spectral elements (Brown and Green, 2002; Henry, 1980). In a multijunction device each element is converted in a material with a different bandgap. This can be implemented in spectrum splitting or stacked cell designs. Figure 2.10 shows loss mechanisms in a double junction, unconstrained device under one Sun illumination. The different shaded areas give the power attributed to different mechanisms and sum to the total power in the solar spectrum. Losses are shown to result in either a reduction in current or voltage determining the form of the current-voltage characteristics. Equations in table 2.1 were used to quantify losses in multijunction devices. Figure 2.11 shows how the fraction of solar radiation lost via different mechanisms changes with varying junction number. Increasing the number of junctions is thermodynamically equivalent to increasing the number of heat engines and as such Carnot, Boltzmann and emission losses increase. In multijunction devices the high energy region of
2.4 Implications for solar cell design

Figure 2.9: Boltzmann loss and output power are shown for fixed $E_g$, which is the optimal $E_g$ in this model for a device under one Sun illumination. Increasing concentration reduces the mismatch between absorption and emission angles and the resulting reduction in Boltzmann loss is directly transferred into power out. Increasing concentration alters optimal $E_g$ at each concentration. This is an artifact of the analytical model used occurring because changes in $E_g$ affect the accuracy of the Boltzmann approximation.
2.4 Implications for solar cell design

Figure 2.10: Intrinsic loss mechanisms are shown for an idealised double junction solar cell with optimal bandgaps and no current matching, under one Sun illumination. As with figure 2.5, the total area of the shaded region describes the power of the incident solar spectrum and the power sacrificed to different intrinsic loss mechanisms is given by the areas of the different shaded regions. Current-Voltage curves for the two junctions are superimposed on the plot. Intrinsic loss mechanisms can then be defined as either current limiting or voltage limiting (Hirst and Ekins-Daukes, 2011).

the spectrum is converted in an absorber with high bandgap, reducing thermalisation losses. Low bandgap materials are used to absorb the low energy region of the spectrum, reducing below $E_g$ loss.

Reducing device temperature and operating voltage will reduce emission loss however, the energy penalty associated with these measures outweighs any potential benefit. One way in which emission loss might be reduced is by overcoming Kirchhoff’s law using a time asymmetric absorber. The application of this non-reciprocal system to photovoltaic devices has been considered by several authors (Green, 2006; Ries, 1983). The Carnot factor will only be
2.4 Implications for solar cell design

**Figure 2.11:** Intrinsic loss mechanisms occurring in a multijunction device, as a function of junction number.

<table>
<thead>
<tr>
<th>number of junctions</th>
<th>power out (analytical)</th>
<th>power out (numerical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (0.98, 1.87 eV)</td>
<td>0.446</td>
<td>0.429</td>
</tr>
<tr>
<td>3 (0.82, 1.44, 2.26 eV)</td>
<td>0.508</td>
<td>0.493</td>
</tr>
<tr>
<td>4 (0.72, 1.21, 1.77, 2.55 eV)</td>
<td>0.546</td>
<td>0.533</td>
</tr>
</tbody>
</table>

**Table 2.3:** The efficiency of multijunction devices calculated using an analytical approach are shown alongside values calculated numerically as shown in Martí and Araújo (1996). Discrepancies of up to 1.7% occur because of approximations made.
eliminated in the limit of an infinite temperature gradient between the Sun and the absorber however, systems with a cooler heat sink such as extra-terrestrial cells will have reduced Carnot loss.

2.5 Summary

Intrinsic losses occurring in a single threshold solar cell under one Sun illumination have been considered in this chapter. Radiation emitted and absorbed by the cell has been evaluated using the generalised Planck equation. By solving this equation analytically the mechanics of intrinsic loss processes become apparent. Five intrinsic loss processes are identified and quantified. Intrinsic losses are shown to cause either a reduction in current or a reduction in voltage, dictating the form of the current-voltage characteristic.

It was found that the optimal operating voltage of a device is limited by an ultimately unavoidable Carnot factor. In converting thermal energy received from the Sun into entropy free electrical work an energy penalty will always be incurred. This loss process is only eliminated in the limit of an infinite thermal gradient between the Sun and the solar cell. A further intrinsic voltage drop is present in solar cells under one Sun illumination. A mismatch between absorption and emission angles causes an expansion of photon modes and a corresponding entropy generation. This loss mechanism is described by Boltzmann’s equation linking available states and entropy generation and its importance can be reduced by solar concentration or emission angle restriction.

In a single junction device, optimal voltage is also limited by the strong interaction between excited carriers and lattice phonons resulting in thermalisation. Third generation designs such as multijunction and hot carrier solar cells impede this loss mechanism. It has been shown that increasing the number of absorbers in a multijunction device decreases thermalisation and below $E_g$ losses but increases the fraction of incident solar radiation lost via Carnot, Boltzmann and emission mechanisms resulting in an overall efficiency increase. Some of the energy lost through thermalisation is recouped because of the mismatch between absorption and emission temperatures ($T_S \neq T_L$). During carrier cooling some entropy is transferred
away from the carrier distribution increasing the free energy available per carrier. This process occurs as a result of degenerate absorption bands and we show that an absorber with discrete energy levels will not experience this free energy advantage. Luminescent emission from the cell reduces the number of available carriers, reducing the operating current however, the primary mechanism of current reduction is the non-absorption of photons with energy below $E_g$.

The cumulative effect of all five intrinsic loss mechanisms are shown to lead to fundamental limits in efficiency. All incident solar radiation is accounted for, creating a complete picture for solar energy conversion in an ideal device. The analytical approach taken shows the effect of varying device design on limiting efficiency. Increasing concentration reduces the fraction of incident solar energy lost via Boltzmann entropy generation resulting in an increase in device efficiency. Other losses as a fraction of incident solar energy are independent of optical étendue. All loss mechanisms however, are shown to be dependent on bandgap.

Solar energy converters can be made to exceed the Shockley Queisser limit and substantial efficiency advantages can be achieved by targeting the dominant intrinsic loss mechanisms with novel device designs.
Hot carrier solar cell concepts

A hot carrier solar cell (HCSC) is a device in which excited carriers are extracted before they fully thermally equilibrate with the surrounding lattice, reducing thermalisation loss and enhancing solar conversion efficiency. There are two key development challenges associated with the HCSC: an absorber material which maintains a hot carrier population under achievable levels of solar concentration, and energy selective contacts to extract hot carriers without incurring an energy penalty.

A photovoltaic solar cell is a heat engine, transferring heat from a hot source (the Sun) to a cold sink (the atmosphere), doing work and generating entropy in the process. The temperature gradient between the source and sink drives the engine. In the case of a non-hot carrier device, the conversion processes following carrier photo-generation are irreversible. The mechanism of carrier cooling generates entropy, leading to a conversion efficiency penalty. In a hot carrier device, energy selective contacts allow for isoentropic cooling, hence thermal energy is converted into chemical potential with Carnot efficiency.
3.1 The hot carrier absorber material

The steady-state carrier distribution temperature is determined by the relative rates of photo-excitation and carrier scattering processes. These critical rates are illustrated in figure 3.1, where carrier distribution is described as a function of time following a pulsed photo-excitation. Prior to photo-excitation only a small thermally excited carrier population exists. Instantaneously after photo-excitation the carrier distribution takes on the shape of the incident photon spectrum. On a sub ps timescale, elastic carrier-carrier interactions re-distribute energy within the excited carrier population to form the distribution with the minimum free energy. This quasi-equilibrium population is described by a temperature ($T_{eh}$), greater than that of the surrounding lattice ($T_L$). On a ps timescale, carriers interact with lattice phonons, dissipating energy to the surrounding lattice, until the carrier population is in thermal equilibrium with the lattice ($T_{eh} = T_L$). While the energy in the carrier population is reduced, the density of the carrier population remains unchanged, assuming non particle conserving interactions to be negligible. This results in quasi Fermi-level splitting and the
3.2 Hot carrier contacts

The structure of an HCSC is illustrated in figure 3.2. The absorber material maintains a hot carrier population relative to the surrounding lattice. In an ideal device no carrier-phonon interaction is considered.

\[ n_{eh}^2 = N_C N_V \exp \left( \frac{-E_g + \mu = 0}{k(T_{eh} > T_L)} \right) = N_C N_V \exp \left( \frac{-E_g + \mu \neq 0}{kT_L} \right) \]  \hspace{1cm} (3.1)

On a ns timescale, carriers recombine radiatively, reducing the density of the excited carrier population, and the corresponding chemical potential, until the carrier population returns to full thermodynamic equilibrium.

A non-hot carrier device operates with a steady-state carrier population in thermal equilibrium but not in chemical equilibrium, as in time period (d) of figure 3.1. A hot-carrier device requires a steady-state carrier population which is not fully thermally equilibrated, as in time period (c) of figure 3.1. This can be achieved by increasing the rate of photo-excitation and reducing the energy loss rate via carrier-phonon interaction.

Figure 3.2: HCSC structure. The HCSC absorber maintains a hot carrier population relative to the surrounding lattice. Carriers are extracted through energy selective contacts, which permit isentropic cooling.
scattering would occur and hence, $\Delta \mu = 0$. This however is an unrealistic expectation for a real world device. Some entropic cooling would occur in the absorber, generating a small $\Delta \mu$. The energy selective contacts allow carriers to thermally equilibrate with the surrounding lattice within a narrow range of states. This generates further chemical potential, with efficiency approaching the Carnot efficiency. This leaves the distribution with chemical potential $e \cdot \Delta V$. While the energy selective contact quenches the hot carrier population in the absorber at the selected energy, sub ps carrier-carrier interactions continually re-populate these levels, ensuring a thermal distribution at all times.

Several authors have considered energy selective contacts. Proof of concept double barrier resonant tunneling structures based on Si quantum dots (Conibeer et al., 2008a) and AlGaAs/GaAs QWs (Yagi et al., 2009) have been demonstrated. Currently these structures suffer from bandwidth issues. High levels of incident power are necessary to produce a hot carrier population in the absorber. For this reason HCSCs are likely to be high current devices and hence require large bandwidth contacts in order to extract carriers. Tunnelling structures by necessity have a limited number of available energy states and therefore bandwidth will be a key challenge in developing double barrier resonant tunnelling structures for energy selective contacts (Le Bris and Guillemoles, 2010). An alternative energy selective contact design, based on optical extraction has been proposed (Farrell et al., 2011). This integrates a hot carrier absorber with a secondary, non-hot carrier solar cell. Photonic engineering allows for quasi-monochromatic optical coupling between components.

### 3.3 Hot carrier models

The HCSC was first modelled using an energy and particle conservation, detailed balance method (Ross and Nozik, 1982). The Ross and Nozik model uses particle conservation to calculate device current (equation 3.2), in a similar way to the Shockley Queisser method discussed in Section 2.2.1. Energy conservation is then employed to determine $\epsilon_{eh}$ for a given
3.3 Hot carrier models

<table>
<thead>
<tr>
<th>Solar conc.</th>
<th>Max efficiency</th>
<th>Optimal T(_{eh}) (K)</th>
<th>Optimal (E_g) (eV)</th>
<th>Optimal (\Delta \mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>one Sun</td>
<td>0.36</td>
<td>3765</td>
<td>0.67</td>
<td>-4.06</td>
</tr>
<tr>
<td>1000 Suns</td>
<td>0.79</td>
<td>3830</td>
<td>0.17</td>
<td>-1.93</td>
</tr>
<tr>
<td>max conc.</td>
<td>0.86</td>
<td>3910</td>
<td>0</td>
<td>-0.74</td>
</tr>
</tbody>
</table>

**Table 3.1:** Optimal \(T_{eh}\), \(E_g\) and \(\Delta \mu\) values with maximum solar energy conversion efficiencies calculated using the Ross and Nozik model.

\(\Delta \mu\), equation 3.3.

\[
J = \int_{E_g}^{\infty} n(E, T_S, 0, \Omega_S)dE - \int_{E_g}^{\infty} n(E, T_{eh}, \Delta \mu, \Omega_C)dE
\]  

(3.2)

\[
J \cdot \epsilon_{eh} = \int_{E_g}^{\infty} E \cdot n(E, T_S, 0, \Omega_S)dE - \int_{E_g}^{\infty} E \cdot n(E, T_{eh}, \Delta \mu, \Omega_C)dE
\]

(3.3)

The chemical potential produced across the device is given in equation 3.4.

\[
e \cdot \Delta V = \Delta \mu \left( \frac{T_L}{T_{eh}} \right) + \epsilon_{eh} \left( 1 - \left( \frac{T_L}{T_{eh}} \right) \right)
\]

(3.4)

In order to balance equations 3.2-3.4 with low bandgap materials \(T_{eh}\) can exceed 6000 K and \(\Delta \mu\) can be negative. These non-physical results are explained by the breakdown of the particle conservation assumption.

Figure 3.3 shows solar conversion efficiency as a function of \(T_{eh}\) and \(E_g\). The corresponding optimal values of \(\Delta \mu\) are also shown. Higher efficiencies are achieved in lower bandgap materials with higher carrier distribution temperatures. However, in this region the optimal values of \(\Delta \mu\) become negative in order to compensate for the high level emission occurring in this regime. The maximum efficiency values stated in table 3.1 are therefore non-physical because they neglect multi-particle scattering.

Würfel (1997) suggests that particle conservation should not be assumed and proposes a detailed balance method using only energy conservation and assuming impact ionisation (Section 1.6.3). The Würfel model assumes \(\Delta \mu = 0\). Substituting this into equation 3.3 gives
3.3 Hot carrier models

Figure 3.3: Solar energy conversion efficiency (top row) and corresponding optimal $\Delta \mu$ values (bottom row) as a function of bandgap and carrier distribution temperature, calculated using the Ross and Nozik HCSC model, under one Sun, 1000 Suns and maximum concentration (left-right).
3.3 Hot carrier models

Figure 3.4: Solar energy conversion efficiency as a function of bandgap and carrier distribution temperature, using the Würfel HCSC model, under one Sun, 1000 Suns and maximum concentration (left-right).

<table>
<thead>
<tr>
<th>Solar conc.</th>
<th>Max efficiency</th>
<th>Optimal $T_{eh}$ (K)</th>
<th>Optimal $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>one Sun</td>
<td>0.53</td>
<td>847</td>
<td>0.91</td>
</tr>
<tr>
<td>1000 Suns</td>
<td>0.71</td>
<td>1335</td>
<td>0.51</td>
</tr>
<tr>
<td>max conc.</td>
<td>0.85</td>
<td>2478</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.2: Optimal $T_{eh}$ and $E_g$ values with maximum solar energy conversion efficiencies calculated using the Würfel model.

Equation 3.5 and reduces the calculation of $\Delta V$ to a simple Carnot equation, equation 3.6.

$$ J \cdot \epsilon_{eh} = \int_{E_g}^{\infty} E \cdot n(E, T_S, 0, \Omega_S) dE - \int_{E_g}^{\infty} E \cdot n(E, T_{eh}, 0, \Omega_C) dE $$  \hspace{1cm} (3.5)

$$ \epsilon \cdot \Delta V = \epsilon_{eh} \left( 1 - \left( \frac{T_L}{T_{eh}} \right) \right) $$  \hspace{1cm} (3.6)

Figure 3.4 shows efficiency as a function of bandgap and carrier distribution temperature, calculated using the Würfel model. Optimal $T_{eh}$ and $E_g$ values and corresponding maximum energy conversion efficiencies are stated in Table 3.2. As seen with the Ross and Nozik model, the Würfel model produces highest efficiencies at low bandgaps however, fixing $\Delta \mu = 0$ incurs a large energy penalty at high values of $T_{eh}$ because of emission, particularly at low concentrations.
3.3 Hot carrier models

The Ross and Nozik model and the Würfel model describe different regimes. When the material bandgap is on the order of \( kT_{eh} \) the effect of impact ionisation and its inverse, Auger recombination, must be considered (Würfel et al., 2005). When multi-particle effects are included \( \Delta \mu \) tends towards zero. Figure 3.5 shows the two different regimes. The region of interest for InGaAs/GaAsP quantum well structures lies in the particle conservation region.

### 3.3.1 Thermalisation coefficient

Both the Ross and Nozik and the Würfel models assume no heat dissipation in the absorber. This is clearly an unrealistic expectation for a hot carrier absorber. For this reason other authors have presented hot carrier models which include the effect of limited entropic thermalisation in the absorber (Le Bris and Guillemoles, 2010; Takeda et al., 2009). The models include an energy loss rate term in the energy conservation equation. This accounts for the rate at which energy is dissipated to the surrounding lattice via carrier-phonon interactions. The carrier energy loss rate \( P_{th} \) is described by equation 3.7 (Ridley, 1991), where \( n \) is the carrier density \( (\text{cm}^{-3}) \), \( t \) is the sample thickness \( (\text{cm}) \), \( h\omega_{LO} \) is the LO phonon energy and \( \tau_{th} \) is the

---

**Figure 3.5:** Particle conservation is only valid when \( E_g >> kT_{eh} \). The shaded region indicates the area of interest for the InGaAs/GaAsP QW material system.
characteristic cooling time.

\[ P_{th} = \frac{tn\hbar\omega_{LO}}{\tau_{th}} \exp\left( \frac{-\hbar\omega_{LO}}{kT_{eh}} \right) \]  \hspace{1cm} (3.7)

Equation 3.7 can be re-written in terms of temperature gradient \( \Delta T = T_{eh} - T_L \) by considering the specific heat of the carrier population \( (C_{eh} = tnk) \) (equation 3.8).

\[ P_{th} = \frac{C_{eh}}{\tau_{th}} \Delta T \exp\left( \frac{-\hbar\omega_{LO}}{kT_{eh}} \right) \]  \hspace{1cm} (3.8)

The thermalisation coefficient \( Q = \frac{C_{eh}}{\tau_{th}} \) (W \cdot K^{-1} cm^{-2}) is defined to allow easy comparison between different material system. Studies show that a \( Q \) less than 10 W \cdot K^{-1} cm^{-2} is required to deliver a hot carrier efficiency advantage under 10,000 Suns concentration (Le Bris and Guillemoles, 2010). The lowest previously reported value of \( Q \), extrapolated from experimental data for \( T_L = 300 \) K, is 77 W \cdot K^{-1} cm^{-2} (Le Bris et al., 2012). This indicates that significant advances in hot carrier absorber design are required in order to develop a high efficiency device. \( Q \) will be used to bench mark samples used in this study, allowing for meaningful comparison between different material systems.

### 3.4 Energy loss rate

Excess kinetic energy of the carrier population is primarily dissipated via phonon emission. In a zinc-blende crystal lattice, such as GaAs, the primitive unit cell contains two atoms. The relative displacement of these atoms describes the vibrational modes of the crystal, figure 3.6. When the two atoms of the primitive unit cell move the in the same direction, a long wavelength oscillation results. The phonons produced are called acoustic phonons, because the oscillating frequency is in the acoustic range. The atoms of the primitive unit cell can also oscillate with opposing motion to produce short wavelength oscillations. In this instance, high frequency optical phonons are produced. Atomic displacement can be parallel or perpendicular.
3.4 Energy loss rate

Figure 3.6: Atomic oscillations in longitudinal optical (LO), longitudinal acoustic (LA), transverse optical (TO) and transverse acoustic (TA) phonon modes.

to the direction of the resulting wave, producing longitudinal (compressional) or transverse (shear) oscillations.

In a polar material, such as GaAs, an additional scattering process must be considered. The partially ionic bonding of the zinc-blende structure results in some charge transfer from the group V element (As), to the group III element (Ga). This charge separation creates a dipole which will oscillate when it is deformed, acting as a scattering potential. A Coulombic restoring force, produced by the dipole, will only be felt in the longitudinal direction. Charges oscillating in the transverse direction will simply slide past each other, not inducing any additional restoring force. Oscillations in the longitudinal direction change the separation of the charges and hence, the restoring force. The dipole oscillation can be either acoustic or optical. Electron scattering along the acoustic branch produces the piezoelectric effect, where as the optical interaction is known as the Fröhlich interaction. Polar-optical interactions are the most important energy relaxation pathway for hot-carriers in polar materials, as it is the dominant interaction mechanisms at temperature $> 60 \text{ K}$, (Yu and Cardona, 2001). Fermi’s golden rule can be used to derive the characteristic carrier-optical phonon interaction time ($\tau_{eh-LO}$) for bulk and quantum well structures, table 3.3. $\alpha$ is called the dimensionless Fröhlich coupling constant and is found to be 0.07 in GaAs (Kent and Wigmore, 2003).
3.4 Energy loss rate

### Bulk Quantum well

\[
\tau_{eh-LO} = \frac{2\alpha}{\omega_{LO}}
\approx 130 \text{ fs in GaAs}
\]

\[
\tau_{eh-LO} = \left(\frac{\pi \alpha \omega_{LO}}{\omega_{LO}}\right)^{-1}
\approx 80 \text{ fs in GaAs}
\]

Table 3.3: Bulk and quantum well electron-optical phonon interaction times, calculated using Fermi’s golden rule

3.4.1 Hot phonon bottleneck

Numerous spectroscopic studies of both bulk and quantum well structures have shown that measured values of hot electron lifetime are approximately an order of magnitude greater than the value of \(\tau_{eh-LO}\) calculated using the simple Fröhlich interaction model (Balkan et al., 1989; Kash and Shah, 1984; Kash et al., 1985; Ryan et al., 1984; von der Linde and Lambrich, 1979). The Fröhlich interaction model assumes a negligible steady-state optical phonon population, which is a valid assumption when optical phonons are in thermal equilibrium with the surrounding lattice. Optical phonons are known to decay via the anharmonic emission of two acoustic phonons. If the optical phonon lifetime \(\tau_{LO-LA}\) is long compared to \(\tau_{eh-LO}\) optical phonons are generated faster than they can decay and distribute their energy through the lattice. This can cause the carrier population to be re-heated by the non-equilibrium optical phonon population and is known as the hot phonon effect.

#### 3.4.1.1 Phononic bandgap

LO phonons decay into two LA phonons via the Klemens mechanism hence, \(\tau_{LO-LA}\) might be extended by inhibiting this interaction. Phonon dispersion can be evaluated using a semi-classical phenomenological model, which assumes a diatomic chain of atoms connected by a restoring force, figure 3.7 (Blencowe, 2001). By only considering nearest neighbours, the equations of motion are given by equations 3.9 and 3.10. The trial solution shown in equation 3.11 is then used to derive a non-trivial solution to the equations of motion given in equation 3.12, where \(\omega\) is the angular frequency and \(k\) is the wavevector. The optical phonon angular frequency at \(k = 0\) can be calculated using Raman spectroscopy (Martienssen, 2005). This value is then used to calculate the value of the restoring force, \(\beta\).
Figure 3.7: A diatomic chain of atoms of masses \( m \) and \( M \), connected by a restoring force \( \beta \). The displacement of the atoms is given by \( U_1 \) and \( U_2 \) with lattice constant \( a \).

\[
m \frac{d^2U_{1, na}}{dt^2} = \beta \left( U_{2, na} - 2U_{1, na} + U_{2, (n-1)a} \right)
\]

(3.9)

\[
M \frac{d^2U_{2, na}}{dt^2} = \beta \left( U_{1, (n+1)a} - 2U_{2, na} + U_{1, na} \right)
\]

(3.10)

\[
U = A \exp(-i(\omega t - kna))
\]

(3.11)

\[
\omega^2 = \beta \left( \frac{1}{m} + \frac{1}{M} \right) \pm \beta \left[ \left( \frac{1}{m} + \frac{1}{M} \right)^2 + \frac{2mM \cos(ka)}{mM} \right]^{\frac{1}{2}}
\]

(3.12)

Dispersion curves calculated using this simple model are plotted in figure 3.8 for GaP, GaAs and InAs. The strain-balanced QW material system investigated in this study is formed of alternating layers of InGaAs and GaAsP, hence, the phonon dispersion across the sample will modulate between GaP-like, and InAs-like behaviour. The atomic masses used in the dispersion curve calculation are shown in table 3.4. The atomic masses of gallium and arsenic are very similar. In the barrier region of the structure, atomically light phosphorus replaces arsenic. The large difference in atomic mass between gallium and phosphorus leads to a
phononic bandgap occurring between optical and acoustic phonon modes. A phononic bandgap also opens up in the well region of the material where heavy indium atoms replace gallium atoms. The introduction of a phononic bandgap inhibits the LO-LA thermalisation pathway, thus enhancing the hot-phonon bottleneck.

3.5 Two-dimensional structures

A confining potential can be introduced in the growth direction of a structure, creating a quantum well (QW) in which carriers are restricted to two degrees of freedom. This is achieved by embedding a narrow (order of an electron wavelength) layer of material with a lower bandgap than that of the surrounding semiconductor into the structure (section 4.1). The effect of confinement is to quantise energy levels in the well region, with the lowest ground state occurring at a higher energy than the bandgap of equivalent bulk material.

The energy of the confined levels is given by the energy eigenvalues \( E_n \) of the time independent Schrödinger equation (equation 3.13) for wavefunctions \( \psi_n \). For a quantum well with width \( L \) and energy depth \( V \), solutions to equation 3.13 for even parity and odd parity states are...
shown below. \( m_w \) and \( m_b \) are the electron effective masses in the well and barrier regions respectively.

\[
\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial x^2} \psi(x) = k \psi(x) \tag{3.13}
\]

\[
k = \begin{cases} 
  k_1 = \frac{\sqrt{2m_w E}}{\hbar} & x < -\frac{L}{2} \\
  k_2 = \frac{\sqrt{2m_w (V-E)}}{\hbar} & -\frac{L}{2} < x < \frac{L}{2} \\
  k_1 = \frac{\sqrt{2m_w E}}{\hbar} & x > \frac{L}{2}
\end{cases}
\]

\[
\psi(x) = \begin{cases} 
  A \exp(k_1 x) & x < -\frac{L}{2} \\
  B_1 \cos(k_2 x) & -\frac{L}{2} < x < \frac{L}{2} \text{ even parity solutions} \\
  B_2 \sin(k_2 x) & -\frac{L}{2} < x < \frac{L}{2} \text{ odd parity solutions} \\
  A \exp(-k_1 x) & x > \frac{L}{2}
\end{cases}
\]

Given that the wavefunction and its derivative must be continuous at the boundary of the well, equations 3.14 and 3.15 can be derived for even and odd parity states respectively.

\[
\frac{m_b}{m_w} k_1 \tan \left( \frac{k_1 L}{2} \right) - k_2 = 0 \tag{3.14}
\]

\[-\frac{m_b}{m_w} k_1 \cot \left( \frac{k_1 L}{2} \right) + k_2 = 0 \tag{3.15}\]

Solutions to equations 3.14 and 3.15 can be found graphically. This is demonstrated for an InGaAs QW embedded in GaAs bulk in figures 3.9 and 3.10. The intersections of line \((m_b/m_w) \tan(k_1 L/2)\) with \(k_2/k_1\) for the even parity states and \((m_b)/(m_w) \cot(k_1 L/2)\) with \(k_2/k_1\) for odd parity states give the energy eigenvalues. In figure 3.9, the well region indium fraction is varied. Increasing indium fraction reduces the well region bandgap and increases
3.5 Two-dimensional structures

The number of confined energy levels. The effect of varying well width is shown in figure 3.10. Wider wells have more confined states, which are closer together.

The density of electron states in a two-dimensional system can be derived in a similar way to the three-dimensional DOS, shown in section 1.4.2.1 however, in two dimensions the volume in momentum space occupied by each state is $\Delta p^2$. This leads to the two-dimensional electron DOS shown in equation 3.16, where $H(E - E_i)$ is the Heaviside function.

$$D_e(E) = 4\pi\frac{m^*}{\hbar^2} \sum_{i} H(E - E_i)dE$$

The two-dimensional DOS is energy independent between energy levels, which produces the step-like DOS shown in figure 3.11, which leads to a step-like absorption profile in ideal QW.
Figure 3.10: Energy eigenvalues are derived graphically for an InGaAs QW embedded in GaAs. Well width fraction is varied.
structures. In real QWs the absorption profile can deviate from this step-like ideal because of interactions between subbands. In addition, excited electrons and holes form bound pairs called excitons as a result of the Coulombic interaction between the oppositely charged carriers. In low dimensional structures this effect is enhanced because of the reduced spatial separation between excited carriers. Excitons couple strongly to incident radiation and hence their effects are evident in the absorption profile of QW structures (Klingshirn, 2007).

3.5.1 Energy loss rates in quantum wells

The effect of dimensionality on carrier cooling rate has been studied by several authors with opposing conclusions published. Some studies find cooling rates to be independent of dimensionality (Leo et al., 1988a,b; Marchetti and Pötz, 1989), while other studies find cooling rates to be much slower in quantum structures, compared to bulk (Pelouch et al., 1992; Ryan et al., 1984). It has been suggested that carrier density \(n_{eh}\) critically determines the dependence on dimensionality (Rosenwaks et al., 1993). Rosenwaks et al. find that energy loss rate is reduced in low dimensional structures, relative to bulk, when \(n_{eh} > 5 \times 10^{17}\) cm\(^{-3}\).
3.5 Two-dimensional structures

Figure 3.12: Carrier density as a function of solar concentration. Equation 2.14 has been used to calculate \( V_{OC} \) developed across a device under concentrated solar illumination. This value is then used in equation 1.28 to calculate the carrier density. This is calculated for a material with \( E_g = 1.3 \text{ eV} \), consistent with GaAs.

It is possible to generate this carrier density in a device illuminated with > 1000 times solar concentration, figure 3.12.

Some authors have published theoretical studies suggesting that nanostructures might be used to form phononic bandgaps through mini-zone folding (Conibeer et al., 2008b). Such materials would rely on an acoustic impedance mismatch between well and barrier materials to cause energy in the acoustic phonon modes to reflect at the interface. The periodicity of the structure causes the interference of back reflections, preventing certain phonon energies from coupling across the well/barrier interface, thus creating phononic mini-gaps. This is analogous to the phononic bandgap formed in a diatomic material with large mass difference between atoms and hence might result in a hot-phonon bottleneck.

For low values of crystal momentum, the free electron, parabolic energy-momentum relationship can be used for electrons in quantum confined energy levels (section 1.4.1). When an electron-LO phonon scattering event occurs energy and momentum must be conserved. This condition restricts the number of permitted interactions and hence influences the rate at which thermal energy is dissipated from the carrier population to the surrounding lattice. Figure 3.13 shows...
3.5 Two-dimensional structures

Figure 3.13: Electron dispersion curves with permitted LO phonon cooling pathways for GaAs/InGaAs QW structures with varying well width and well region indium content. Left: $L = 10 \text{ nm}$, 10% indium. Right: $L = 20 \text{ nm}$, 20% indium.

electron dispersion curves for a shallow, narrow well (10% indium, $L = 10 \text{ nm}$) and a deep, wide well (20% indium, $L = 20 \text{ nm}$). Arrows indicate permitted LO phonon interactions, which conserve energy and momentum, with an electron in the second confined energy level with zero momentum.

In the case of the narrow, shallow well the energy separation between the first and second confined energy levels is greater than the LO phonon energy and hence the electron can transition from the second to the first energy level by emitting an LO phonon, losing energy in the process. In the case of the wide, deep well, this energy separation is less than the LO phonon energy and hence for an electron to transition into the first energy level it must absorb an LO phonon, increasing the energy of the carrier distribution. The zig-zag line in figure 3.13 represents LA phonon scattering. The confined energy level separation in the wide, deep well sample requires more carrier energy to be dissipated via carrier-LA phonon interaction, than the narrow, shallow well. Electron-LA scattering is much slower than electron-LO scattering, further reducing the energy loss rate in the wide, deep well.

Dür et al. (1996) use an ensemble Monte Carlo simulation to show that in QWs containing two subband energy levels, where the energy separation between the two subbands is less than that of an optical phonon, slow carrier cooling occurs. Murdin et al. (1997) use ps pump-probe...
techniques to show that in a quantum well with subband energy separation less than the LO phonon energy, initially after photo-excitation, hot carriers have sufficient kinetic energy to emit an optical phonon and transition from the second subband energy level to the ground state of the well. As the distribution starts to cool fewer carriers are sufficiently energetic to emit an LO phonon. Carriers can only decay from the second energy level via slower acoustic phonon interaction, creating a bottleneck in the cooling pathway.

3.6 Energy balance rate model

The carrier population can be described by an energy balance rate equation. The rate at which the energy of the carrier distribution changes \( (dE/dt) \) can be related to rate of change in carrier distribution temperature \( (dT_{eh}/dt) \) through equation 3.17. Specific heat is given by \( 3/2nk \) in a 3D structure and \( nk \) in a 2D structure, where \( n \) is the carrier density (Kent and Wigmore, 2003).

\[
\frac{dE}{dt} = C_{eh} \frac{dT_{eh}}{dt}
\]  

(3.17)

In a device at \( V_{OC} \), when no electrical power is extracted, \( dE/dt \) is the difference between absorbed optical power \( (P_{abs}) \) and the power thermalised \( (P_{th}) \), equation 3.18 (Ridley, 1991). This assumes that the rates of radiative and non-radiative recombination are slow compared to \( P_{abs} \).

\[
C_{eh} \frac{dT_{eh}}{dt} = P_{abs}(t) - P_{th} = P_{abs}(t) - \frac{C_{eh}}{\tau_{eh-LO}}(T_{eh} - T_{LO}) \exp\left(\frac{-E_{LO}}{kT_{eh}}\right)
\]  

(3.18)

The rate at which the energy of the LO phonon population changes can be analogously described (equation 3.19). The rate at which energy is supplied to the LO phonons is \( P_{th} \). This energy is finally dissipated to the LA phonon population with rate \( P_{LO-LA} \), determined
by the specific heat of the LO phonons ($C_{LO}$) and the rate of LO-LA phonon scattering ($\tau_{LO-LA}$). Equation 3.19 allows hot phonon effects to be considered.

$$C_{LO} \frac{dT_{LO}}{dt} = P_{th} - P_{LO-LA}$$
$$= \frac{C_{eh}}{\tau_{eh-LO}} (T_{eh} - T_{LO}) \exp \left( \frac{-E_{LO}}{kT_{eh}} \right) - \frac{C_{LO}}{\tau_{LO-LA}} (T_{LO} - T_{LA})$$ (3.19)

Specific heat is dependent on carrier density hence, rate equations describing electron (equation 3.20) and hole (equation 3.21) populations are required in order to solve equations 3.18 and 3.19. $N_{opt}(t)$ and $N_{th}$ are the rates at which carriers are optical and thermally generated, respectively. $N_{rad}$ is the rate of radiative recombination. $n_c$ is the number of conduction band electrons, $n_v$ is the number of valence band holes, $n_i$ is the intrinsic carrier density (equation 1.24) and $B$ is the bio-molecular rate of recombination.

$$\frac{dn_c}{dt} = N_{opt}(t) + N_{th} - N_{rad}$$
$$= N_{opt}(t) + B \cdot n_i^2 - B \cdot n \cdot p$$ (3.20)

$$\frac{dn_v}{dt} = N_{opt}(t) + N_{th} - N_{rad}$$
$$= N_{opt}(t) + B \cdot n_i^2 - B \cdot n \cdot p$$ (3.21)

$T_{eh}$ can be calculated as a function of time using equations 3.18-3.21. Starting conditions $n = nD$, where $nD$ is the background doping level, $p = n_i^2 / nD$ and $T_{eh} = T_{LO} = T_{LA}$ were applied.

The temporal evolution of carrier and LO phonon temperature is calculated for a 1 $\mu$m thick GaAs sample and is shown in figure 3.14. After $t = 0$, the sample is illuminated with CW
3.6 Energy balance rate model

Figure 3.14: $T_{eh}$ as a function of time for a 1 $\mu$m thick GaAs sample. 532 nm CW illumination with power density 1000 W $\cdot$ cm$^{-2}$ starts at time = 0. $C_{LO}/C_{eh} = 100$. Orange and green lines refer to $T_{LO}$ and $T_{eh}$ respectively.

532 nm light with power density 1000 W $\cdot$ cm$^{-2}$. This is roughly equivalent to 10,000 Suns. $C_{LO}/C_{eh} = 100$ and the values of $\tau_{eh-LO}$ calculated using the Fröhlich interaction model (table 3.3) were selected for demonstration.

Initially, the optical generation of carriers ($N_{opt}(t)$) leads to an increase in carrier density and a corresponding increase in $C_{eh}$ and $C_{LO}$ (equations 3.20-3.21). In addition, the power absorbed by the carrier population ($P_{abs}$) leads to an increase in $T_{eh}$ (equation 3.18). The rate at which the carrier energy is then dissipated to LO phonons ($P_{th}$) is described by the characteristic cooling rate $\tau_{eh-LO}$. Eventually, $P_{th}$ becomes greater than $P_{abs}$. At this time $dE/dt$ becomes negative and $T_{eh}$ starts returing to equilibrium.

$P_{LO-LA}$ is determined by the characteristic cooling time $\tau_{LO-LA}$, equation 3.19. With $\tau_{LO-LA} > \tau_{eh-LO}$ hot LO phonons result in carrier re-heating. The effect of varying $\tau_{LO-LA}$ is shown in figure 3.14, with an enhanced re-heating effect demonstrated for larger values of $\tau_{LO-LA}$. Eventually, $P_{LO-LA}$ exceeds $P_{th}$ and the carrier and LO phonon populations both return to equilibrium. This occurs as $dn/dt \to 0$ and the rate of photon emission reaches the rate of photon absorption. At this time a steady state carrier distribution temperature is achieved. Larger values of $\tau_{LO-LA}$ result in a slight increase in steady state $T_{eh}$.

According to Einstein statistics $C_{LO} = k \cdot n_q$, where $n_q$ is the number of excited LO phonon states (Mandl, 1971). For a non-equilibrium LO phonon population, $T_{LO}$ is not known and hence $C_{LO}$ is not easily estimated (Le Bris et al., 2012). In figure 3.15 the effect of varying
3.6 Energy balance rate model

![Graph showing energy balance rate model](image)

**Figure 3.15:** $T_{eh}$ as a function of time for a 1 $\mu$m thick GaAs sample. 532 nm CW illumination with power density $1000 \text{ W} \cdot \text{cm}^{-2}$ starts at time = 0. $\tau_{LO-LA} = 100 \text{ ps}$ is used. Orange and green lines refer to $T_{LO}$ and $T_{eh}$ respectively.

$C_{LO}$ as a function of $C_{eh}$ is shown. For a fixed change in phonon distribution energy, a system with a lower specific heat will exhibit a greater temperature change than a system with a higher specific heat. Consequently, systems with lower specific heat achieve higher steady state $T_{eh}$.

The effect of varying incident power is shown in figure 3.16. A 1 $\mu$m thick GaAs sample is compared to a sample with the 10 nm thick InGaAs QW grown into GaAs buffer with total thickness 1 $\mu$m. Photon absorption in both samples is approximately the same however, in the case of the QW sample excited carriers diffuse into the well region. Volumetric carrier density is therefore higher in the case of the QW sample. Total carrier capture in the QW is assumed, however, in real world samples, the fraction of carriers captured in the well will depend on carrier diffusion length, well depth and well thickness. In figure 3.16 it is shown that higher incident powers produce higher steady state values of $T_{eh}$. The enhanced carrier density in the QW samples leads to a substantial increase in steady state $T_{eh}$.

Figures 3.14-3.16 show that variables $\tau_{LO-LA}$, $C_{LO}$ and $P_{abs}$ are important in determining steady state $T_{eh}$ and hence the suitability of a material system as a hot carrier absorber.
3.6 Energy balance rate model

Figure 3.16: $T_{eh}$ as a function of time for a 1 $\mu$m thick GaAs sample and a 10 nm InGaAs QW. 532 nm CW illumination starts at time = 0. $\tau_{LO-\text{LA}} = 100$ ps and $C_{LO}/C_{eh} = 100$ is used. Orange and green lines refer to $T_{LO}$ and $T_{eh}$ respectively.
Samples were grown in order to investigate hot carrier effects in QW structures. The samples were designed to evaluate the effect of a range of well features on hot carrier behaviour. Parameters which were systematically varied include; well number, well depth and well width. These samples were grown using metalorganic vapour phase epitaxy (MOVPE) at the University of Tokyo. Details of the sample structures are given in this chapter. Various spectroscopic techniques were employed to study these samples including; continuous-wave photoluminescence and ultra-fast time resolved photoluminescence spectroscopy. The design and assembly of the laboratory represents a significant component of the work completed. This chapter discusses the experimental techniques, particularly where novel solutions were developed.
4.1 III-V semiconductors

Solar cells can be made from elemental semiconductors such as Si, however, by forming compound semiconductors from two or more elements materials with desirable solar cell characteristics can be engineered. Alloys formed of group III and group V elements are frequently used in opto-electronic devices, including solar cells. GaAs is a III-V semiconductor, which can be grown as a substrate and has a direct bandgap making it a strong absorber. The relative quantities of different components can be adjusted in compounds formed of 3 or more elements allowing manipulation of bandgap and lattice constant. Energy wells are introduced into a structure by depositing layers of semiconductor with different energy bandgaps. When the width of these layers is on the order of the electron wavelength quantum effects are observed. Adding In to GaAs forms a material with a lower bandgap however, the atomic separation also increases. Growing a narrow layer of InGaAs embedded in GaAs will produce a quantum well however, the variation in lattice constant introduces mechanical strain into the sample.

The larger atomic spacing of the InGaAs leaves the well region compressively strained. Inevitable relaxation of that strain produces broken bonds and material dislocations which

---

**Figure 4.1:** The lattice constant of binary III-V semiconductor materials are shown as a function of bandgap. Circles indicate binary compounds and lines indicate ternary compounds. Solid lines and dotted lines describe direct and indirect bandgap materials respectively. A strain-balanced InGaAs/GaAsP quantum well lattice is also illustrated.
act as recombination centres. Such a structure has poor material quality and therefore will
never be able to produce ultra-high efficiency. A solution can be to introduce other elements
to form compounds which are lattice matched to GaAs, such as Al. Unfortunately this is a
difficult material to work with because it readily oxidizes, similarly producing materials with
defects, increasing non-radiative recombination pathways and reducing efficiency. Previous
studies have successfully shown hot carrier cooling in QW structures however, this has always
been in material systems which are susceptible to defects and hence are unsuitable candidates
for HCSC device development.

4.1.1 Strain-balancing

The lattice matching of bandgap engineered material is a complex materials problem, however,
in recent years a compelling solution has been developed. Strain-balancing is a growth
technique whereby layers of oppositely strained barrier materials are grown either side of the
energy well to fully compensate the strain in the well region, preventing relaxation. In the case
of InGaAs, GaAsP can be used as a barrier region material because it has a lattice constant
which is lower than GaAs and it therefore experiences tensile strain when grown on GaAs.
The thickness of the barrier region is adjusted to ensure the compressive strain in the well
region is fully compensated by the tensile strain in the barrier region. Strain-balancing allows
stacks of quantum wells to be grown without dislocations occurring, producing samples with
excellent material quality, which might realistically be used to develop ultra-high efficiency
devices. Figure 4.1 shows bandgap as a function of lattice constant for a range of different
semiconductors. A strain-balanced InGaAs/GaAsP quantum well lattice is illustrated.

4.2 Sample structures

Samples used in this study were provided by the Sugiyama group at RCAST, University of
Tokyo. Samples with a range of different well parameters were produced, table 4.1. In the
first instance samples were designed for an initial growth run to achieve two key objectives:
demonstrate a hot carrier effect in InGaAs/GaAsP and, if a hot carrier effect was observed,
Table 4.1: An overview of samples used in this study. Detailed structure information is given in Appendix B.

<table>
<thead>
<tr>
<th>sample name</th>
<th>well depth</th>
<th>well number</th>
<th>well width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I1</td>
<td>shallow 11%In</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>I2</td>
<td>shallow 11%In</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>I3</td>
<td>deep 20%In</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>I4</td>
<td>deep 20%In</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>O1</td>
<td>very deep 25%In</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>O2</td>
<td>very deep 25%In</td>
<td>20</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 4.2: Different regions of the sample structures.

provide a guide to structure optimization. With these objectives in mind, samples were designed to be conservative by modern growth capabilities, to ensure excellent material quality.

Single well and corresponding 10 well structures were grown with a moderate phosphorus fraction in the barrier region (9%) and 8 nm well width. The wells were also grown in a substantial GaAs buffer region and capped with passivating, high bandgap InGaP window layers, figure 4.2. The purpose of the GaAs buffer is to prevent indium from the InGaP window layer contaminating the GaAsP barrier. Carrier density is one of the key parameters in generating a hot carrier effect and therefore it was necessary to design a structure in which non-radiative recombination pathways were minimised. This would give the best chance of observing a hot carrier effect in the strain-balanced InGaAs/GaAsP system. In order to meet the second objective and provide a guide to structure optimisation, samples were grown with two different well region indium fractions: 11% and 20%.
After characterising a hot carrier effect in the initial growth run and identifying mechanisms for improving the structure, samples were designed for a second optimisation run. Samples were grown much more aggressively, with 25% indium in the well region and 33% phosphorus in the barrier. The effect of varying well width was also investigated. Structures with 7 nm and 14 nm well widths were compared. The growth of these highly strained structures was made possible by the innovative growth techniques employed at the University of Tokyo. In situ reflectivity measurements allowed the accumulation of strain to be monitored during crystal growth, ensuring sharp interfaces and uniform wells (Wang et al., 2011).

### 4.3 Continuous-wave photoluminescence spectroscopy

Hot carrier effects were investigated using a range of spectroscopic techniques to identify hot carrier characteristics of the transient and steady-state electron-hole populations. Under continuous-wave (CW) illumination, the photo-excited carrier population forms a steady state thermal distribution. The shape of the emitted photoluminescence (PL) spectra describes this thermal distribution. The temperature of the steady-state carrier distribution is determined by the relative rates of three key parameters: carrier generation, carrier-phonon scattering and carrier-recombination (Section 3.1). CWPL was performed for a range of incident intensity in order to vary the rate of carrier generation.

The CW source used to perform CWPL was a Spectra Physics millennia V laser. This diode-pumped Nd:YVO4 source produces up to 5 W of 532 nm coherent laser light. This source was chosen because its high output power generates high carrier densities in the samples. The output power can also be incremented in steps of 1 mW.

For a 6000 K black body, the average wavelength of above bandgap photons is in the range 530-590 nm for the given samples, Figure 4.3. This range of wavelengths occurs because the samples used in this study have a range of different indium content and a corresponding range of bandgaps. A monochromatic light source, in this wavelength regime, incident on a sample, supplies approximately the same energy and the same number of carriers to the electron-hole population, as the Sun under a given concentration. Away from this wavelength regime, for a
4.3 Continuous-wave photoluminescence spectroscopy

Figure 4.3: The average wavelength of above bandgap photons in a 6000 K blackbody is given as a function of bandgap. This is calculated to be 530-590 nm for the given samples (shaded area). The available 532 nm laser (green line) is at the lower limit of this range.

given carrier density, the energy flux delivered to the carrier population will deviate from what would be expected from the concentrated solar illumination. Whilst a monochromatic source can never be used to directly imitate a broadband source, using a laser wavelength in this regime would allow for meaningful comparison with realistic solar cell operating conditions. The wavelength of the millennia V sits at the lower limit of the calculated range and therefore is suitable for these measurements.

The CWPL set-up was assembled with the laser at normal incidence to the sample, figure 4.4. This technique allows a highly focusing microscope object to be used as both the focusing and the collection optic, enabling ultra-high incident photon flux density, \((8000 \text{ W} \cdot \text{cm}^{-2})\). The monochromator available was a Princeton Instruments Acton 2500. This has a long path length (25 cm) allowing for fine spectral resolution, but only a single grating and so can suffer from stray light. The normal incidence arrangement is particularly susceptible to laser light entering the monochromator and so to prevent this light from scattering into the measured spectra, a longpass filter was necessary.
4.3 Continuous-wave photoluminescence spectroscopy

Figure 4.4: Normal incidence PL experimental set-up. The sample was mounted on a heat sinked XYZ stage. The 532 nm laser was focused into the sample using a 20X microscope objective. Radially emitted PL is efficiently captured by the microscope objective and focused into the monochromator using a lens of the correct numerical aperture. Any reflected or scattered laser light is prevented from entering the monochromator using a longpass filter. The CMOS camera and Oriel fibre light source are used for calibration, and removed during PL measurements.

The surface of the sample was illuminated with an Oriel fibre source and the sample position was then adjusted parallel to the axis of the microscope objective until an image of the sample surface could seen on the Thorlabs CMOS camera. The laser power incident on the sample was measured using a laser power meter. In order to determine the incident photon flux density, the laser spot size also had to be measured. This was achieved by imaging the laser spot into the camera. The bitmap image of the laser spot was processed in Octave, which is an open source interpreted language with extensive graphics capabilities, and a script was written to count any pixel with intensity > half the maximum intensity. The pixel area was calibrated by imaging a 100 µm aperture with the same optical path, allowing the laser spot area to be quantified, figure 4.5.
4.4 Absorption coefficient characterisation

4.4.1 Density dependent photoluminescence excitation measurements

The shape of the absorption coefficient can be determined as a function of wavelength using a technique called photoluminescence excitation (PLE) spectroscopy. This technique, however, does not give an absolute value of absorption coefficient. A variable wavelength light source such as a lamp or scanning laser is used to photo-excite the sample. A Ti:sapphire laser was used in this instance. As the excitation wavelength is scanned over the region of interest the PL emission at a fixed wavelength is measured. The intensity of the PL is proportional to the density of excited carriers and hence, an increase in absorption coefficient will increase the measured signal, mapping out the shape of the absorption coefficient.

Carrier density is an important parameter to consider when measuring hot carrier effects, with high carrier density regimes producing the hottest distributions. An experimental setup was designed and assembled to perform density dependent PLE, allowing the effect of high carrier density on absorption coefficient to be observed (Figure 4.6). The Millennia V laser output was split along two paths. Approximately 90% of the source was used to pump the Ti:sapphire laser and the remainder was used to optically bias the sample. A microscope slip was used as a beam splitter because it was thin enough to prevent deviation of the transmitted beam but also has a high damage threshold and hence, can tolerate the full 5 W supplied by the Millennia V.

Figure 4.5: a) 3D Intensity plot of a laser spot, imaged using Thorlabs CMOS camera. b) Image of a 100 µm aperture used to calibrate pixel size.
4.4 Absorption coefficient characterisation

**Figure 4.6:** The Ti:sapphire laser, incident on the sample is scanned in wavelength to determine relative absorption coefficient. The sample is also optically biased using some of the millennia V output. A computer controlled neutral density filter wheel is used to vary the incident intensity of the pump beam. A Cryostat is used to allow low temperature measurements.

The output power of the millennia V was always set at 5 W, because high pump power is required to achieve the full range of Ti:sapphire wavelengths. In order to vary the intensity of the incident pump beam a computer controlled neutral density filter wheel was purpose built from a stepper motor and controller. A fixed neutral density filter was used on the output of the Ti:sapphire laser to ensure the probe was low powered. The Ti:sapphire beam was then chopped to allow the PL produced as a result of the probe beam to be extracted from the large background DC signal produced from the pump excitation of the sample. The two beams were then combined using a dichroic mirror which reflected the Ti:sapphire beam and transmitted the 532 nm pump beam.

It is desirable to make PLE measurements using a cryostat because the quantum well exciton and subband energy levels are particularly sharp at low temperature. The geometry of the cryostat prevented the use of the microscope objective as a focusing and collection optic. In addition, the PLE measurement is particularly sensitive to scattered laser light because often the detection wavelength will be very close to the wavelength of the laser light. For this reason a glancing angle geometry was assembled, whereby the laser excitation is incident...
4.4 Absorption coefficient characterisation

on the sample away from the normal. The reflected laser beam therefore does not enter the monochromator. Despite the surface of the sample being highly polished, significant laser light was still scattered off the surface of the sample. This scattered laser light was sufficient to totally distort the measured signal, particularly close the detection wavelength. PLE spectroscopy in the literature is performed using a double grating spectrometer, eliminating this unwanted laser scatter. In order to perform PLE using only a single grating monochromator, a bandpass filter was placed in front of the entrance slit.

The wavelength of the bandpass filter was selected to coincide with the detection wavelength. This set-up is sensitive to the sharpness of the filter cut-off because of the necessity for discrimination between the ti-sapphire laser excitation wavelength and the detection wavelength. Interference filters were used because adjusting the angle of the filter gives some flexibility in the transmitted wavelengths. In addition, this type of filter is available with sharper transmission cut-off than dye filters.

Control software was written in the C programming language to automate the PLE measurement. The lock-in-amplifier, monochromator and ND wheel stepper motor were controlled via RS232 and the laser stepper motor via its own computer card.

4.4.2 Transmission spectroscopy

Transmission spectroscopy can be used to make an absolute measurement of material absorption coefficient ($\alpha(E)$) below the bandgap of the sample substrate. Because of the substrate thickness the transmission of above bandgap photons is negligible. The absorption coefficient was determined by measuring wavelength dependent transmission through a sample and comparing this to the transmission through a GaAs control grown on the same wafer with the same InGaP surface window layer. $\alpha(E)$ can be calculated from transmission spectroscopy using equation 4.1, which is derived from Beer’s Law. $I_s(E)$ and $I_c(E)$ are the optical intensities measured after the sample and the control respectively. The thickness of the absorbing material is denoted by $x$, which is taken to be the thickness of InGaAs, for sub
4.5 Time resolved photoluminescence spectroscopy

![Diagram of the transmission spectroscopy set-up.](image)

**Figure 4.7:** Transmission spectroscopy set-up.

GaAs bandgap photo-excitation energies.

\[
\alpha(E) = -\ln \left( \frac{I_s(E)}{I_c(E)} \right) \frac{1}{x}
\]  

(4.1)

To improve signal to noise the set-up was designed to maximise \( I_s(E) \) and \( I_c(E) \), figure 4.7. The wafers used in this study were not double polished, resulting in scattering at the rear-surface of the sample. For this reason the sample was positioned close to the detector in order to collect as much of the transmitted light as possible. In addition, high quality reflecting lenses were used in the optical path to maximise light incident on the sample.

### 4.5 Time resolved photoluminescence spectroscopy

Several time resolved photoluminescence (TRPL) spectroscopy methods were employed to investigate hot carrier dynamics: upconversion photoluminescence, streak camera and time correlated single photon counting (TCSPC). The upconversion photoluminescence system uses an ultra-fast (150 fs) pulse to photo-excite the sample and as an optical gate for detection, it therefore provides both short duration excitation and excellent temporal resolution detection.

The streak camera system also used an ultra-fast excitation pulse (140 fs) but has slower detection temporal resolution (20 ps). The TCSPC system has a long duration excitation pulse (750 ps) and slower detection temporal resolution (300ps). Other experimental factors including spectral resolution and pulse energy were different for the three systems. These factors determine what regimes the different systems could be used in.
4.5 Time resolved photoluminescence spectroscopy

4.5.1 Ultra-fast time resolved upconversion photoluminescence spectroscopy

Ultra-fast carrier dynamics can be investigated by exciting carriers using an ultra short mode locked excitation pulse and observing the resulting PL at set time intervals following the excitation. Upconversion spectroscopy in this study was performed during a visit to the University of Sydney. The experimental set-up used is shown in figure 4.8. This set-up has a pulsed Ti-sapphire source with 1 kHz repetition rate, 150 fs pulse duration and output pulse energy > 2 mJ. The output is split along two optical paths, one for photo-excitation and one for optical gating. Each path passes through an optical parametric amplifier (OPA). The dual OPA system allows the laser wavelength along each path to be independently tuned. PL from the sample is incident on a upconverting crystal with the optical gate pulse. The frequency sum of the PL and the optical gate is then detected through a double monochromator using a highly sensitive PMT. Altering the position of the delay stage in the optical gate path delays the arrival of the gate pulse at the crystal. In this way the time period following the photo-excitation event can be probed with 150 fs resolution.

4.5.2 Streak camera photoluminescence spectroscopy

Longer time scale carrier dynamics can be probed using a streak camera. In this study, streak camera measurements were taken during a visit to the University of Kobe. The experimental set-up used is shown in figure 4.9. A pulsed Ti-sapphire source with 80 MHz repetition rate, pulse duration 140 fs and output pulse energy > 1.6 nJ was used. The laser light was then passed though a pulse picker, to allow the repetition rate to be varied, before being focused onto the sample. The NIR streak camera used in this study was uniquely produced by Hamamatsu for the University of Kobe and is sensitive in the wavelength range 1000 - 1700 nm. The camera has a temporal resolution of 20 ps and captures images at a rate of 20 MHz. Photons entering the streak camera are incident on a photo-cathode, producing a beam of electrons which are accelerated through a cathode ray tube. An electric field deviates the path of the beam and the resulting streak pattern is detected on a CCD array, providing temporal resolution.
4.5 Time resolved photoluminescence spectroscopy

Figure 4.8: Upconversion PL spectroscopy set-up at the University of Sydney
4.5 Time resolved photoluminescence spectroscopy

![Diagram of streak camera TRPL set-up at the University of Kobe](image)

**Figure 4.9:** Streak camera TRPL set-up at the University of Kobe

### 4.5.3 Time correlated single photon counting

Longer time scale carrier dynamics can also be investigated using TCSPC. A TCSPC set-up was assembled at Imperial College, as shown in figure 4.10. Samples were photo-excited using a pulsed laser diode. The diode driver had a repetition rate of 5 - 80 MHz. Pulse duration varied with power, figure 4.11. At maximum power the FWHM pulse duration was measured as 0.75 ns and the output energy per pulse was measured to 0.16 nJ. The resulting PL was passed through a monochromator and detected using a NIR PMT. The time which elapsed between the detection of a photon and the following pulse was recorded by the data acquisition system. Individual photon counts were then deposited into time histogram bins and the characteristic transient PL is accumulated at a maximum rate of one count per pulse, although in practice considerably slower than this. The PMT transit time spread (TTS) is the variation in time between a photon being detected by the photocathode and the PMT anode outputing a pulse. TTS limits the temporal resolution of the system, in this case to 300 ps.
4.5 Time resolved photoluminescence spectroscopy

Figure 4.10: TCSPC set-up.

Figure 4.11: Pulse intensity as a function of time for a range of pulse powers. Max pulse power delivers 0.16 nJ per pulse. FWHM pulse duration measured to be 0.75 ns.
4.5 Time resolved photoluminescence spectroscopy

4.5.4 Comparing TRPL laser systems

The different TRPL systems employed in this study use different lasers for photo-excitation. In order to compare the results taken on these different systems and presented in the literature, carrier density must be considered. Different density metrics are sometimes used:

- **Photon flux density** \((\text{cm}^{-2}\text{s}^{-1})\) is the rate at which photons are incident on a sample, during a pulse, divided by the laser spot area. This parameter is comparable to the unit \(\text{W}\cdot\text{cm}^{-2}\) used for CW spectroscopy in this study.

- **Pulse photon density** \((\text{cm}^{-3})\) is the volumetric density of photons in a given pulse. This unit is often used in TRPL studies and is calculated by dividing incident photon flux density by the speed of light.

- **Well carrier density** \((\text{cm}^{-3})\) is the volumetric carrier density within the well region of the sample. This is the product of pulse duration and the rate of carrier absorption \((\text{cm}^{-2}\text{s}^{-1})\), calculated using Beer’s law, divided by well region thickness. At 780 nm, photon absorption occurs throughout the samples (well, barrier and buffer regions) and hence the full sample thickness is used to calculate the rate of carrier absorption. 100% carrier capture into the well region is then assumed. On short time scales radiative recombination can be neglected.

These density metrics were calculated for the different laser systems (table 4.3). The laser parameters used in these calculations are shown in table 4.2. Laser spot size is critical for all of the density metrics. Both the Sydney and Kobe ti-sapphire laser excitation was incident at a glancing angle to the sample and hence these systems have larger spots. The IC pulsed diode system was implemented in direct incidence alignment with a microscope objective in order to increase incident photon flux density. Despite the small spot size, this system has the lowest incident photon flux because of the the long pulse duration. The Sydney ti-sapph laser has the largest spot size but still produces the highest incident photon flux density. This occurs because of the very low pulse repetition rate. Each pulse produced by this system is highly energetic. Smaller spot sizes were used to produce even higher incident photon flux density.
<table>
<thead>
<tr>
<th>Power (mW)</th>
<th>rep. rate (MHz)</th>
<th>pulse duration (ps)</th>
<th>spot radius (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sydney ti-sapph</td>
<td>10</td>
<td>0.001</td>
<td>0.15</td>
</tr>
<tr>
<td>Kobe ti-sapph</td>
<td>1300</td>
<td>80</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>80</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>80</td>
<td>0.14</td>
</tr>
<tr>
<td>IC pulsed diode</td>
<td>1.6</td>
<td>10</td>
<td>750</td>
</tr>
</tbody>
</table>

Table 4.2: Laser excitation parameters for the three different pulsed laser systems used in this study.

<table>
<thead>
<tr>
<th>Photon flux (cm$^{-2}$s$^{-1}$)</th>
<th>Pulse photon (cm$^{-3}$)</th>
<th>Well carrier (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sydney ti-sapph</td>
<td>$2 \times 10^{28}$</td>
<td>$8 \times 10^{17}$</td>
</tr>
<tr>
<td>Kobe ti-sapph</td>
<td>$3 \times 10^{26}$</td>
<td>$9 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>$6 \times 10^{25}$</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>$6 \times 10^{24}$</td>
<td>$2 \times 10^{14}$</td>
</tr>
<tr>
<td>IC pulsed diode</td>
<td>$5 \times 10^{23}$</td>
<td>$2 \times 10^{13}$</td>
</tr>
</tbody>
</table>

Table 4.3: Comparing photon and carrier density metrics.

but this resulted in sample damage. The density metric which is significant in generating a hot carrier population is the well carrier density. The long pulse duration of the IC pulsed diode is beneficial in producing high well carrier density because all incident photons in a pulse contribute. The rate at which photons are absorbed is not important as long as the rate of photo-excitation is fast compared to the rate of radiative recombination.

4.6 Data analysis

Carrier distribution temperature was calculated by fitting a straight line to the natural log of the measured intensity, as a function of energy, in the high energy tail region of the emitted PL spectrum. This method for determining distribution temperature has precedence in the literature (Shah and Leite, 1969). The high energy tail region of the photoluminescence spectrum is required because in this region the absorption coefficient of the material varies
slowly, compared with the exponential behaviour of the Fermi-Dirac distribution. In quantum well structures the absorption coefficient at energies close to the confined energy levels will be rapidly varying and hence, cannot be used to determine temperature. The 2D density of states (DOS) can be generally derived using the Heaviside function. This results in a sharp step-like DOS function. In the case of many QW systems this is a poor approximation to the actual material DOS because it neglects the non-parabolic effects of valence state mixing. In the strain balanced InGaAs/GaAsP QW structure the well region is compressively strained. This causes the splitting of heavy and light hole bands, which reduces in-plane state mixing (Khan et al., 2001). It is therefore expected that the absorption coefficient of the samples used in this study should be similar to the ideal step-like function. The absorption coefficient in the energy region between higher energy confined states should be relatively flat, allowing high energy tail fitting.

The high energy tail fit was performed using a Gnuplot fit function. This least-squares fitting algorithm requires accurate initial values of the fitting variables for rapidly varying functions. For this reason, the data was manipulated to allow a straight line fit, rather than fitting an exponential function. The gradient of the straight line corresponds to $1/kT_{eh}$.

Several different detectors were used in this study to cover the full range of emission wavelengths from the different samples. The wavelength dependent sensitivity of the detector changes the shape of the spectra, consequently changing the calculated temperature. Newport 818-SL and 818-IR detectors were used for much of the CW detection. These detectors were calibrated at NIST in 10 nm wavelength steps. EQE calibration files with 1 nm steps were produced for these detectors using linear interpolation, and were used to correct the intensity measurements. Calibration files were produced for the other detectors used in the experiments, by comparing spectra taken using the two calibrated Newport detectors.

During the course of this study carrier distribution temperature was calculated for more than 1000 spectra. A series of wrapper scripts were written in order to process this large volume of data. These scripts corrected for the wavelength dependence of the detector, converted wavelength data supplied by the spectrometer software into energy units and called Gnuplot fit and plot functions in order to produce the analysis presented.
TRPL has a 3D parameter space: intensity, time and wavelength. Many spectroscopic investigations use wavelength resolution to select an energy transition and then time resolution to observed radiative decay of that energy transition. Dynamic hot carrier investigations are more experimentally time intensive because the objective is to observe a change in spectral shape as a function of time. Accumulating counts over the full time and wavelength ranges of interest is a time consuming process and as such, the hardware resolution was carefully considered during the experimental process to ensure the best use of available lab time. Temporal resolution and counts per wavelength step could then be traded subsequently during the data analysis.

Analysis software was written in the C programming language to selectively collect data into time histogram bins, improving the counts per wavelength step and thus reducing the uncertainty in carrier distribution temperature, calculated with high energy tail fitting. This technique was critical in reducing the uncertainty in calculated temperatures but required a sacrifice in temporal resolution, figure 4.12.

Figure 4.12: A comparison of carrier distribution temperatures calculated as a function of time, with and without using time histogram analysis software.
Samples were characterised using continuous wave photoluminescence (CWPL) spectroscopy. The shape of the emitted photoluminescence spectra describes the photo-excited carrier population distribution. This allows the temperature of the carrier distribution to be determined and hence, any hot carrier effect to be identified.

5.1 Characterisation of the initial growth run

Samples from the initial growth run were first characterised using the set-up described in section 4.3. A 532 nm laser was used for photo-excitation. This wavelength of light is absorbed throughout the sample, in both bulk GaAs and well regions. The intensity of the incident laser light was varied and measurements were taken at 294 K.
Figure 5.1: Photoluminescence spectra as a function of incident power density, normalised to the well region emission peak. Top: I1. Bottom: I3.
5.1 Characterisation of the initial growth run

The contour plots in figure 5.1 show the resulting photoluminescence spectra as a function of the incident power density. The emission peak at 870 nm is from the GaAs buffer. The emission peak for I1 occurs at 943 nm. The I3 sample has deeper wells, and has an emission peak at 1007 nm. The spectra in figure 5.1 are normalised to the peak of the well region emission. The shape of the well region spectra can be seen to broaden with increasing incident power density. This broadening indicates heating of the carrier distribution.

The temperature gradient between the carrier distribution and the surrounding lattice is critical to the efficiency of an HCSC device. It is therefore critical to differentiate between carrier heating and lattice heating. Both non-equilibrium carrier heating and lattice heating will result in a broadening of the photoluminescence spectra. Lattice heating, however, will also induce a red shift in the peak of the photoluminescence spectra, as the energy bandgap of the material narrows. This occurs because the lattice distribution temperature is determined by the LA phonon population. As shown in figure 3.6, LA phonons are propagating waves and form the anharmonic component of the atomic binding energy, hence an increase in the amplitude of the LA vibrations leads to increased atomic separation. This is commonly known as thermal expansion and results in a reduction in the electron binding potential, in turn reducing the energy bandgap of the material. The emission peaks in figure 5.1 do not shift with increased incident power density, indicating that the broadening is a result of non-equilibrium carrier heating.

This heating effect can be quantified using high energy tail fitting (section 4.6). In order to identify slowly varying regions of the absorption coefficient, where high energy tail fitting can be applied, transmission spectroscopy was performed (section 4.4.2). Absorption in the well region of the single well structures was very low and hence 10 well MQW samples with matching indium fraction and well width were used to determine absorption coefficient.

Calculated absorption coefficients are shown in figure 5.2. For the 11% (I1) and the 20% (I3) indium samples the lowest energy level exciton peaks occur at 934 nm and 1006 nm respectively. This is compatible with the emission peaks observed in the photoluminescence spectra, allowing for a small Stokes shift. In both samples a region of slowly varying absorption coefficient is clearly identifiable between the peak of the exciton and the on-set of GaAs
5.1 Characterisation of the initial growth run

Figure 5.2: Energy dependence of absorption coefficient for samples I2 and I4.

Absorption. In these regions the gradient of the photoluminescence spectra, when plotted logarithmically, corresponds to $1/(kT_{eh})$. This linear fit is shown in figure 5.3.

The linear fit function in Gnuplot was used to calculate carrier distribution temperatures for all measured spectra. The fitting procedure is discussed in section 4.6. The uncertainties in the calculated temperatures were determined by how well the data corresponded to the linear fit. Calculated temperatures for samples I1 and I3 are shown in figure 5.4.

Figure 5.3: Photoluminescence spectra for the lowest and highest incident power densities measured. A linear fit is made in the high energy region of the emission, where absorption coefficient is slowly varying. Left: I1. Right: I3.
5.1 Characterisation of the initial growth run

5.1.1 Density dependent PLE measurements

Exciton broadening effects have been observed in QW structures with high carrier density (Chemla et al., 1984; Miller et al., 1999, 1982). This broadening mainly derives from phase space filling, Coulomb screening and Coulomb broadening. It has been suggested that exciton broadening might change the gradient of the absorption coefficient under high incident power density (Führer et al., 2008). The absorption coefficient must vary slowly for the high energy tail fitting to be used to calculate carrier distribution temperature. Transmission measurements were used to determine appropriate energy regions for fitting, however, these measurements only show the absorption coefficient at low carrier density. Density dependent PLE was performed to ensure that high energy tail fitting is a valid method for calculating carrier distribution temperature under high carrier density.

Figure 5.5 shows PLE measurements of sample I2 for a range of optical biasing. The experimental set-up used is discussed in section 4.4.1. Values of $T_{eh}$ calculated using high energy tail fitting are given. Corresponding PLE measurements are shown for the same optical bias values. PLE measurements were obtained by fixing the monochromator on the lower energy tail of the sample emission and scanning the ti-sapphire laser over the main exciton
5.1 Characterisation of the initial growth run

![Graph showing PL and PLE measurements of sample I2.](image)

Figure 5.5: PL (solid line) and PLE (dots) measurements of sample I2, taken for a range of incident power densities. Calculated values of $T_{eh}$ are shown for each measurement. $T_L = 140$ K.

and high energy tail of the emission. A lattice temperature of 140 K was used for these measurements because a sharp bandpass filter, which would transmit the detection wavelength and block the excitation wavelength was available.

Exciton bleaching can be seen in figure 5.5. As the incident power is increased, the relative intensity of the exciton decreases, suggesting that the oscillator strength is reduced at higher carrier density. As incident power is varied a small change in the gradient of the absorption coefficient is observed in the high energy tail region of the emission. Over the temperature fitting region the absorption coefficient changes by a factor of 1.1 in the case of low power illumination and 1.5 in the case of high power illumination. The PL emission intensity over this region changes by well over an order of magnitude. It is therefore reasonable to conclude that the absorption coefficient is sufficiently slowly varying to permit the use of high energy tail fitting for both low and high incident powers.

5.1.2 Observations from the initial growth run characterisation

As can be seen in figure 5.4, above approximately 1000 W · cm$^{-2}$ (equivalent to approximately 10,000 Suns) the carrier distribution can no longer dissipate heat to the LA phonon population.
5.2 Characterisation of the optimisation growth run

fast enough to maintain thermal equilibrium with the surrounding lattice. A hot carrier population in quasi thermal equilibrium is therefore observed. This result satisfies the primary object of this study, outlined in section 4.2: observing, for the first time, a hot carrier effect in the strain-balanced InGaAs/GaAsP QW system.

The incident power densities required to demonstrate hot carrier effects in these samples are well beyond the range that is achievable in a real world concentrator photovoltaic (CPV) module. Optimisation of the structure is therefore required to obtain an enhanced hot carrier effect.

Two key observations were made from the CWPL spectroscopy of the initial growth run samples, in order to guide device structure optimisation:

1. Increasing the incident power density and hence, the rate at which energy is supplied to the carrier distribution, increases the steady state carrier distribution temperature. This observation is consistent with the rate model outlined in section 3.1.

2. Under the same level of incident power density, the measured values of $T_{eh}$ are higher in the deep well sample (I3) than in the shallow well sample (I1).

The first key observation highlights the importance of carrier density in the well region of the sample. In the optimised structures the thickness of surface GaAs buffer material is minimised to increase well region absorption. The second key observation indicates that increasing indium content further, to create very deep wells, might further enhance the observed hot carrier effect. The strain-balancing of the InGaAs/GaAsP material system allows stacks of deep QWs to be grown without the introduction of lattice defects. This feature was exploited in the optimisation growth run.

5.2 Characterisation of the optimisation growth run

Key conclusions from the initial growth run were implemented in the optimisation growth run. In addition, the effect of well width was investigated.
5.2 Characterisation of the optimisation growth run

CWPL was performed on the optimised structures: O1 and O2. The Si detector was not suitable for characterising these structures because the wells’ high indium content red shifts the peak of the emission to a wavelength greater than 1µm where Si is no longer sensitive. For this reason a cooled InGaAs array was used for PL detection. Photoluminescence spectra for the optimised samples are shown in figure 5.6 as a function of incident power density. Well region emission peaks are observed at 1027 nm and 1075 nm for O2 and O1 respectively. In the case of the wide well sample (O1) an additional higher energy bound state is also observed. As with the initial growth run samples, the spectra broaden with increasing incident power density. There is no corresponding red-shift in the emission peak wavelength indicating that the broadening can be attributed to non-equilibrium hot carrier effects, and not lattice heating.

Transmission spectroscopy was performed on the optimised sample structures, figure 5.7. For the narrow (O2) and the wide (O1) well samples the lowest energy level exciton peaks occur at 1030 nm and 1078 nm respectively. As with the samples in the initial growth run, this is compatible with the emission peaks observed in the photoluminescence spectra, allowing for a small Stokes shift.

Energy regions with slowly varying absorption coefficient were identified from the transmission spectra, to allow carrier distribution temperature to be quantified, using high energy tail fitting. The gradient of the PL emission was determined using the linear fit function in Gnuplot, as discussed in section 4.6, figure 5.8. Calculated carrier distribution temperatures for the optimised grown run are shown alongside those from the initial grown run in figure 5.9, as a function of incident power density.

5.2.1 Observations from the optimisation growth run characterisation

An enhanced hot carrier effect is observed in both samples from the optimisation growth run, compared to the initial growth run. In the case of the wide well sample (O1) the improvement is dramatic. A temperature gradient between the carrier population and the surrounding lattice > 150 K is measured under 1400 W · cm⁻² incident power density.
5.2 Characterisation of the optimisation growth run

Figure 5.6: Photoluminescence spectra as a function of incident power density, normalised to the well region emission peak. Top: O2. Bottom: O1.
5.2 Characterisation of the optimisation growth run

Figure 5.7: Energy dependence of absorption coefficient for samples O1 and O2.

Figure 5.8: Photoluminescence spectra for the lowest and highest incident power densities measured. A linear fit is made in the high energy region of the emission, where absorption coefficient is slowly varying. Left: O2. Right: O1.
5.3 Photo-excitation directly into the wells

It is well established in the literature that QW structures exhibit an enhanced hot carrier effect over bulk material (Rosenwaks et al., 1993). As well width increases, density of states becomes more bulk-like, and therefore it might be expected that highly confined structures would produce the hottest carriers however, this result disagrees with that hypothesis. The thick well sample exhibits a greatly enhanced hot carrier effect over the narrow well sample.

5.3 Photo-excitation directly into the wells

Carriers can be photo-excited directly into the well region of the sample by selecting a wavelength beyond the absorption threshold of GaAs (870 nm at 300 K). The 532 nm excitation better describes the performance of a device under solar illumination however, the 920 nm excitation can provide insight into underlying mechanisms. With the available sample set, using both initial and optimised growth runs, four structural characteristics were varied: thickness of GaAs buffer layer, indium fraction, well width and well number. The 920 nm excitation allows the effect of these variations to be separately evaluated.

CWPL with direct well region excitation was performed using the experimental set-up discussed in section 4.3. Calibrated Si and Ge detectors were used. The resulting PL spectra from
5.3 Photo-excitation directly into the wells

samples I3, I4, O2 and O1 are shown in figure 5.10. Energy regions with slowly varying absorption coefficient, where high energy tail fitting can be applied are marked on each curve in black. The calculated temperatures are compared with the 532nm excitation case in figure 5.11.

To observe similar carrier distribution temperatures, higher incident power densities are required with a 920 nm laser excitation compared to a 532 nm excitation. This is to be expected because the absorption coefficient is much greater at 532 nm than at 920 nm for all layers of the structures, leading to comparatively higher absorbed power density at 532 nm. Under both 532 nm and 920 nm illumination, the optimisation sample O1 produced the
5.3 Photo-excitation directly into the wells

![Graph showing carrier distribution temperatures as a function of incident power density.]

**Figure 5.11:** Carrier distribution temperatures calculated using high energy tail fitting as a function of incident power density. 532 nm and 920 nm photo-excitation are compared.

The greatest hot carrier effect.

New insight can be derived by comparing the carrier distribution temperatures achieved in samples I3 and O2 under the different illumination sources. With 532 nm excitation, the optimisation sample O2 outperforms the initial growth run sample I3. This is not the case under 920 nm excitation, indicating that the hot carrier enhancement observed in the optimisation sample O2 under 532 nm illumination derives from the increase of well region absorption through the removal of the surface GaAs buffer.

In figure 5.11, the initial growth run samples I4 and I3 are compared with direct well region excitation. These samples have different well numbers and also different surface GaAs buffers however, under 920 nm excitation the surface buffer is transparent allowing for direct evaluation of the effect of well number. For a given incident power density, hotter carriers are observed in the single well sample. The effect of well number is further investigated by plotting $T_{eh}$ as a function of absorbed power density, figure 5.12. At 920 nm the GaAs wafer is transparent, allowing the absorption coefficient to be experimentally determined using transmission spectroscopy, figures 5.2 and 5.7. Using the known absorption coefficient and well region thickness, Beer’s law can be applied to determine absorbed power density ($P_{abs}$). It is clear from figure 5.12 that single well sample I3 produces hot carriers at lower absorbed power.
5.3 Photo-excitation directly into the wells

![Graph showing carrier distribution temperatures](image)

**Figure 5.12:** Carrier distribution temperatures calculated using high energy tail fitting as a function of absorbed power density.

densities than corresponding MQW sample I4. Absorption is exponentially dependent on sample thickness, hence photons are absorbed more rapidly in the first QW, with subsequent QWs contributing progressively fewer carriers to the total number absorbed. The volumetric carrier density in the single well sample is higher than that of the corresponding MQW sample because the MQW sample has a greater well region volume. This does not, however, mean that a single well sample is necessarily desirable as a hot carrier absorber. Ultimately, the solar power conversion efficiency of a device is defined per unit area and hence, a thin sample which produces hot carriers by allowing significant photon transmission will never achieve high efficiency. A comparison can also be drawn between optimisation samples O1 and O2. These samples have identical total well material thickness and hence the volumetric carrier densities should be similar, with only a small discrepancy caused by slight differences in absorption coefficient. The striking difference in the carrier distribution temperatures for a given $P_{\text{abs}}$ can only be explained by the difference in individual well thickness.
5.4 Calculating thermalisation coefficient

With the measured values of $P_{abs}$ a carrier thermalisation coefficient $Q$ (W·K$^{-1}$cm$^{-2}$) can be derived for each of the materials, as discussed in section 3.4. This coefficient is equivalent to the ratio of carrier specific heat and carrier cooling time and can be used to calculate the rate at which heat energy dissipates away from the photo-excited carrier population ($P_{th}$), equation 3.8.

In a steady state, when no electrical power is extracted, the optical power absorbed ($P_{abs}$) by the carrier population is equal to the sum of the power re-radiated and the power thermalised. Power dissipated via radiative recombination is small compared with the $P_{abs}$, figure 2.6, and hence need not be included in the rate equation, leaving the relation $P_{abs} = P_{th}$. Using this relation in equations 3.7 and 3.8, $n/\tau_{th}$ can be calculated as a function of $\Delta T$, figure 5.13. $Q$ is proportional to the gradient of the resulting linear relation. Calculated values are shown in table 5.1.

Le Bris and Guillemoles (2010) report that $Q < 10$ W·K$^{-1}$cm$^{-2}$ would be required to gain a hot carrier efficiency advantage in a device under 10,000 Suns concentration. While 10,000 Suns is not achievable in a real world PV module, 10 W·K$^{-1}$cm$^{-2}$ is considered to be a
5.4 Calculating thermalisation coefficient

<table>
<thead>
<tr>
<th>Sample</th>
<th>Q (W · K$^{-1}$cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I3</td>
<td>9.53 ± 0.63</td>
</tr>
<tr>
<td>O1</td>
<td>20.06 ± 0.85</td>
</tr>
<tr>
<td>O2</td>
<td>131.93 ± 11.52</td>
</tr>
<tr>
<td>I4</td>
<td>230.41 ± 13.68</td>
</tr>
</tbody>
</table>

Table 5.1: Calculated values of thermalisation coefficient for samples I3, O1, O2 and I4.

suitable target Q value for developing a proof of concept HCSC. The lower the Q value the slower the energy loss rate. GaSb-based heterostructures have been characterised in this way. The lowest reported Q value for this system is 77 W · K$^{-1}$cm$^{-2}$ (Le Bris et al., 2012). Samples I3 and O1 characterised in this study have surpassed this threshold. Both samples exhibit Q values on the order of the 10 W · K$^{-1}$cm$^{-2}$ target.

Caution should be taken when interpreting these results because the Q factor is proportional to absorbing layer thickness. Total absorption thickness should be small to produce low Q but must be large to generate high current in a device and produce good energy conversion efficiency. Sample I3 has absorber thickness = 8 nm and consequently only absorbs approximately 1.5% of the incident light at 920 nm, according to Beer’s law. Sample O1 has total absorber thickness = 140 nm. This results in much greater absorption, approximately 23% of the light at 920 nm, making this a much more attractive option for developing a proof of concept device.

One way in which the balance between low Q factor and good absorption might be addressed is by investigating other mechanisms for increasing absorption without increasing well region thickness. Q factors here have been calculated by exciting carriers directly into the wells using 920 nm excitation, below the bandgap of the GaAs buffer. In a solar cell, excitation will be broadband with much of the absorption occurring in the GaAs buffer. Many of the carriers absorbed in the buffer will be captured into the well region. This is demonstrated in figure 5.1 where 532 nm excitation is used. In this instance the majority of light incident on sample I3 will be absorbed in the 750 nm GaAs buffer. The resulting PL shows much stronger emission from the well region of the sample, with a comparatively small peak at the GaAs bandgap (870 nm). This indicates that many of the carriers absorbed in the buffer region end up in the well region, increasing the volumetric carrier density in the wells and slowing the energy loss.
rate. Further improvements might also be achieved by using front or rear surface structures. A distributed Bragg reflector (DBR), tuned to the well region absorption effectively doubles the optical path length without increasing the well region thickness (Johnson et al., 2005). Scattering structures, such as front surface Al disks, also improve optical path length (Li et al., 2012).
Time resolved photoluminescence spectroscopy

6.1 Optical gate TRPL

Samples from the initial growth run were characterised using optical gate upconversion spectroscopy. The experimental set-up used is discussed in section 4.5.1. The results presented were collected during a six week visit to the University of Sydney.

TRPL from sample I4 at 77 K is shown in figure 6.1. From this data, carrier distribution temperature was calculated as a function of time using high energy tail fitting. The fitting regions selected are shown in figure 6.2. Only 3 data points were available per fit because the Sydney set-up has limited spectral resolution.

Spectral resolution is fundamentally limited because of the very short pulse duration of the
**Figure 6.1:** Photoluminescence spectra as a function of time after photo-excitation for sample I4 at 77 K. The well region emission peak occurs at 940 nm. Linear interpolation was used to smooth the contour plot.

**Figure 6.2:** Photoluminescence spectra at fixed times after photo-excitation for sample I4 at 77 K. Data have been grouped into time bins to improve the spectral resolution in the fitting region. Times stated in the key refer to the centre of the time histogram bins and are given in units of picoseconds.
laser used as an optical gate. This is because of the uncertainty principle, stated in equation 6.1.

\[ \Delta E \Delta t \geq \hbar \]  

The pulse duration was 150 fs, which corresponds to a wavelength uncertainty of 2.15 nm at 780 nm. In addition, the repetition rate of the laser was relatively low, and hence long acquisition times were required to accumulate sufficient spectral data, particularly on the high energy tail, away from the main emission peak.

The spectral resolution was further compromised by the proximity of the bulk GaAs and the well region emission peaks. Radiative recombination in the GaAs bulk was very rapid, compared to the well region. This made it difficult to resolve the bulk and well region emission peaks at short time scales, particularly in the shallow well samples, where the peaks are closer together. The delay stage length also prevented any measurements beyond 2 ns after photoexcitation, when well region emission would have dominated. This is demonstrated in figure 6.3, where radiative decay curves for bulk and well region emission are compared for sample I4. Initially, the bulk region emission is dominant because of the faster rate of radiative recombination. The high energy tail lies between the bulk and well regions, hence resolving the peaks is essential for evaluating carrier thermalisation.

These complications were partly mitigated by taking measurements at low temperature, making the emission peaks sharper. In addition, data were grouped into time bins to produce radiative decay histograms (Section 4.6). By compromising temporal resolution, the number of photon counts per fit is increased, improving the statistical quality of the fit. These measures allowed time resolved PL from the deep MQW sample I4 to be acquired and analysed. The optimisation samples were not available when these measurements were performed.

The photo-excitation pulse used to obtain the data shown in figure 6.1 was highly energetic (Section 4.5.4) and as such, could induce some localised heating of the lattice in the region of the laser spot. The wavelength of the well region emission peak in figure 6.1 was compared
Figure 6.3: Comparison of bulk and well region emission from sample I4 at 77 K.

Figure 6.4: Photoluminescence from sample I3 at 80 K, under low levels of CW photo-excitation.
with the well region emission peak in figure 6.4. This shows PL taken from sample I3 at 80 K, with a very low incident power density and consequently no carrier heating. The two peaks occur in similar places, 950 nm in figure 6.4 and 940 nm in figure 6.1. The slight discrepancy can be attributed to small unintentional variations in sample structure and a 3 K lattice temperature difference. If local lattice heating were occurring with the highly energetic pulse, a substantial red shift in well region emission peak would be observed in figure 6.1 relative to the well region emission peak in figure 6.4. This is because local lattice heating induces thermal expansion (Section 5.1).

Temperatures as a function of time after photo-excitation are shown in figure 6.5. The hot carrier distribution observed can be fully attributed to slowed carrier cooling, rather than hot lattice effects. Temperatures > 2000 K are measured at time < 100 ps after photo-excitation and the distribution remains hot beyond 2 ns. The cooling curve is characterised by two distinctive behaviours, with rapid cooling at times < 200 ps, followed by slower cooling. These rates have been quantified by fitting a bi-exponential function to the data, using Matlab. The energy balance rate model discussed in section 3.6 produces bi-exponential cooling behaviour when a hot phonon effect occurs.
6.2 Streak camera TRPL

The streak camera set-up, described in section 4.5.2 was used to characterise hot carrier dynamics in samples O1, O2 and I4. This set-up does not suffer from the uncertainty principle limit to spectral resolution because the ultra-fast pulse used for photo-excitation is not used for detection.

Figure 6.6 shows photoluminescence as a function of wavelength and time. The photo-excitation wavelength used was 920 nm. This wavelength is only absorbed in the well region of the sample. Incident photon flux is varied to observe the effect of well region carrier density on carrier distribution temperature.

The camera captures a 20 ns time window. With a laser repetition rate of 80 MHz, two pulses are captured in each frame. The long radiative lifetimes of the optimisation samples relative to the initial grown run sample I4 are clearly visible in figure 6.6. Long lived carriers are an indicator of excellent material quality, with few non-radiative recombination centers.

In figure 6.6 the first pulse is detected at time 3-6 ns. This variation in pulse start time occurs because neutral density filters were used to limit the light intensity entering the monochromator, to protect the streak camera. Changing the filters changes the optical path length between the sample and the monochromator entrance, delaying the pulse arrival time by a different amount. When analysing this data, the time axis is shifted such that the peak intensity of the PL emission is taken at time zero. This allows comparison between measurements.

Figure 6.7 shows the streak camera spectra at selected time intervals after time zero. The high energy tail fitting regions are shown. The data has been collected into time bins consisting of 8 data sets, reducing the temporal resolution of data from 20 ps to 160 ps. This was necessary to improve to quality of the high energy tail fitting. Wavelength steps have also been grouped into bins consisting of 4 data sets. While this increases the count number per data point plotted in figure 6.7 thus reducing the noise on the plotted spectra, it does not increase the number of counts per fit and hence has no effect on calculated temperatures.
6.2 Streak camera TRPL

(a) Photo-excitation with 920 nm producing well region carrier density $\sim 1 \times 10^{17}$ cm$^{-3}$.

(b) Photo-excitation with 920 nm producing well region carrier density $\sim 3 \times 10^{16}$ cm$^{-3}$.

(c) Photo-excitation with 920 nm producing well region carrier density $\sim 3 \times 10^{15}$ cm$^{-3}$.

Figure 6.6: Streak camera images showing photon counts as a function of wavelength and time. Incident photon flux density is varied to produce a range of well region carrier densities. Left: sample O1. Mid: sample O2. Right: sample I4.
Despite careful data processing, noise on the data remains a problem. For this reason, only a selection of time intervals are shown in figure 6.7 so that trends in the data can be visualised. The spectral peaks narrow as a function of time for high carrier density, indicating carrier cooling. At low carrier densities the gradients in the high energy tail region are steep, relative the high carrier density case, and change very little as a function of time. The carrier distribution temperatures calculated from the high energy tail fitting for all time intervals are shown in figure 6.8.

For the highest well region carrier density ($\sim 1 \times 10^{17}$ cm$^{-3}$) the wide well optimisation sample O1 outperforms samples O2 and I4, with hot carriers detected out to 4 ns. Beyond 4 ns, insufficient counts are recorded to allow high energy tail fitting. At this high carrier density, hot carriers are also observed in samples O2 and I4. I4 only produces sufficient photon counts out to 2 ns because of the short radiative lifetime in this sample. When carrier density is reduced to $\sim 3 \times 10^{16}$ cm$^{-3}$ carrier distribution temperatures are also reduced, with samples O2 and I4 producing carriers only marginally above the lattice temperature. No hot carriers are observed if the carrier density is reduced to $\sim 3 \times 10^{15}$ cm$^{-3}$, only slightly above the background doping level of the samples.

Each 3D data set was recorded with 20 min acquisition time. A longer acquisition time would be necessary to increase the number of photon counts per fit, improving the quality of the high energy tail fits and consequently the uncertainty on the calculated temperatures. With smaller uncertainty, carrier cooling rates could be reliably derived from the time dependent temperatures plotted in figure 6.8. Collecting data for hot carrier analysis is lab time intensive. For this reason, methods of investigating hot carrier dynamics with readily available facilities at Imperial College were pursued. While the Imperial College TCSPC system could only provide 300 ps temporal resolution, the very long lived (> 4 ns) hot carriers detected using the streak camera system indicate that interesting hot carrier dynamics might still be observable with the TCSPC system.
6.2 Streak camera TRPL

(a) PL spectra at selected time intervals for sample O1.

(b) PL spectra at selected time intervals for sample O2.

(c) PL spectra at selected time intervals for sample I4.

Figure 6.7: PL spectra at given time intervals (ns) showing high energy tail fitting regions with solid lines. Data has been collected into time bins to increase the number of counts per fit and hence improve the quality of the fits. Not all time intervals are shown. Well region carrier densities (left-right) $\sim 1 \times 10^{17}, 3 \times 10^{16}, 3 \times 10^{15}$ cm$^{-3}$.
Figure 6.8: Carrier distribution temperatures for samples O1, O2 and I4. Well region carrier densities (top-bottom) $\sim 1 \times 10^{17}$, $3 \times 10^{16}$, $3 \times 10^{15}$ cm$^{-3}$
6.3 Time correlated single photon counting

Samples I4, O1 and O2 were characterised using TCSPC, with the set-up discussed in section 4.5.3. Measurements were taken at 295 K. Spectra are shown in figure 6.9. A slower repetition rate was selected for samples O1 and O2 because these both exhibited very long radiative lifetimes and hence the pulse appears to start at a different time to sample I4. In order to analyse these data, the time scale is shifted such that time zero occurs at the end of the laser pulse. These measurements were taken using long acquisition times (300 s per wavelength step). Accumulating a full spectrum for a single sample takes $\geq 4$ hours however, the large number of counts is necessary for high energy tail fitting. Even with the high count number, time histograming was employed to analyse TCSPC data (section 4.6). Time steps were collected into groups of 16, reducing temporal resolution from the 20 ps available from the photon counting electronics, to approximately 300 ps which matches the temporal resolution of the PMT. The high energy tail fits for these samples are shown in figure 6.10.

Several interesting spectral features are observed in figure 6.10. In sample O1, a second higher energy well transition is visible in the spectra. Initially, the peak of the higher energy well transition is greater than the peak of the main exciton however, at longer times, the peak of the main exciton starts to dominate. In addition, spectra taken during the pulse (negative time intervals) show a suppression of emission from the main exciton, in all three samples. This might be an observation of carriers being captured into the well and descending into the lowest energy state.

Several studies have shown that intersubband carrier scattering rates are critical in determining the rate of carrier cooling (Dür et al., 1996; Murdin et al., 1997). These studies show that narrow subband energy level separation can restrict LO phonon emission resulting in slowed carrier cooling, as discussed in section 3.5.1. The subband energy separation in a QW will be smaller in wider wells (section 3.5). The two subband levels observed in the PL from the wide well sample O2 (figure 6.10) are separated by approximately 65 meV. The LO phonon energy of the well region of the sample is between 31 and 36 meV. The LO phonon energy of InAs is 31 meV and that of GaAs is 36 meV. Carriers in the second energy level clearly have sufficient
6.3 Time correlated single photon counting

Figure 6.9: TRPL spectra taken using TCSPC. Top: I4. Middle: O2. Bottom: O1.
Figure 6.10: PL spectra at set time intervals after the end of the excitation pulse. Negative times refer to time intervals after the start of the pulse but before the end of the pulse. High energy tail fitting regions are marked with a black line. Top: I₄. Middle: O₂. Bottom: O₁.
6.3 Time correlated single photon counting

energy to emit an LO phonon. In addition these measurements were taken at 295 K hence at values of $\Delta T > 100$ K electrons should have sufficient thermal energy to emit an LO phonon. Sample O1 is therefore not directly comparable with the Dürr et al. (1996) and Murdin et al. (1997) studies however, the presence of a highly populated second energy level in sample O1 might indicate that the rate of intersubband scattering is a significant factor in carrier cooling.

Temperatures calculated from these high energy tail fits are shown in figure 6.11. The hottest carriers are observed in the O1 sample. This is consistent with the CWPL measurements which show sample O1 has the lowest thermalisation coefficient (Table 5.1). Both samples O1 and I4 show bi-exponential cooling behaviour, suggesting that two interaction mechanisms, with different characteristic lifetimes are occurring. Initially, a large temperature gradient is generated in both of these samples. The rate of cooling is characterised by the gradient of the cooling slope in figure 6.11. Rapid cooling in both samples occurs on a short time scale $< 1$ ns. On a longer time scale, the temperature gradient reduces and the rate of cooling slows. In sample O1, this second rate is much slower than the corresponding rate in sample I4. As a result, a hot carrier population is sustained out to 4 ns in sample O1 whereas I4 cools in half that time.

Sample O2, never achieves $\Delta T > 100$ K and the cooling behaviour is described by a single exponential. In the CWPL measurements sample O2 produced hotter carriers than sample I4, although only marginally. Comparing the cooling slope gradients of these two samples provides new insight. It is clear that, at short time scales I4 is able to produce very hot carriers, however, its CW performance is compromised by fast carrier cooling at longer time scales, relative to sample O2. While large temperature gradients are not achieved in sample O2 at short time scales, this sample produces hotter CW carriers because it has very slow cooling over longer time scales.

It should be noted that the gradient of the cooling slope for sample O2 is very similar to that of sample O1 after 1 ns. These two samples have the same well region indium content and barrier region phosphorus content, consequently optical and acoustic deformation potentials and phonon dispersion should be comparable in these samples. The similarity in cooling rates observed in samples O2 and O1 on longer timescales ($> 1$ ns), suggests that the limiting
6.3 Time correlated single photon counting

Figure 6.11: The temperature gradient between carrier and LA phonon distributions, as a function of time interval after the end of the photo-excitation pulse. A bi-exponential function describes the behaviour of samples O1 and I4, whereas sample O2 shows single exponential behaviour. Fitting functions are shown with a solid line.

The mechanism in the cooling pathway for this regime is the LO-LA phonon interaction rate because phonon dispersion will be approximately the same for both samples (section 3.4.1). This is indicative of a hot phonon bottleneck.

The short time scale cooling behaviour in these samples is quite different. In this regime it is possible that the carrier-LO phonon interaction is dominating the carrier cooling. The difference in well width of these samples results in very different electron dispersion (Section 3.5) and hence different carrier-LO phonon scattering lifetimes. It is the short timescale carrier-LO phonon interaction that ultimately leads to a hotter steady state carrier distribution in sample O1, relative to sample O2, and not the LO-LA interaction rate because this is the same for both samples.

6.3.1 Analysis and context

Time constant $\tau_{th}$, described in equation 3.7, can be used to characterise energy loss rates, allowing for quantitative comparison with different samples. Rosenwaks et al. (1993) refer to this time constant as $\tau_{avg}$. From equations 3.7 and 3.17, $\tau_{th}$ can be calculated as shown in
6.3 Time correlated single photon counting

equation 6.2.

\[ \tau_{th} = \frac{-\hbar \omega_{LO}}{k \frac{dT_{eh}}{d\tau}} \cdot \exp \left( -\frac{\hbar \omega_{LO}}{k T_{eh}} \right) \]  \hspace{1cm} (6.2)

d\frac{T_{eh}}{dt} \text{ is calculated by fitting exponential and bi-exponential functions to the measured data and then differentiating these functions. Calculated values of } \tau_{th} \text{ are shown in figure 6.12 for samples O1, O2 and I4 alongside data taken from the paper Rosenwaks et al. (1993). This paper presented carrier cooling measurements of bulk GaAs and MQW GaAs samples for a range of carrier densities. The higher carrier density used in the Rosenwaks study is comparable to the carrier density used in TCSPC measurements of samples O1, O2 and I4.}

The low carrier density measurements from the Rosenwaks study produce relatively short cooling lifetimes in both bulk and MQW samples. At higher carrier density, the bulk sample \( \tau_{th} \) only improves slightly, whereas \( \tau_{th} \) calculated for the GaAs MQW sample increases by approximately an order of magnitude. The cooling behaviour of the Rosenwaks MQW sample is similar to sample I4 in the low \( \Delta T \) regime. Samples O1 and O2 have very similar characteristic cooling lifetimes in the low \( \Delta T \) regime, as previously discussed this might be because of their similar P:As and In:Ga ratios in the barrier and well regions.

While \( \tau_{th} \) is a useful parameter for comparing samples, it does not relate to the interaction rate of any physical mechanism. This is because equation 3.7 only considers energy transfer from carriers to LO phonons and does not consider the reverse process. As \( T_{eh} \) approaches \( T_{LO} \) the rate of energy transfer slows because the temperature gradient between the two populations reduces. By including energy transfer from LO phonons back to carriers, a characteristic lifetime that describes the carrier-LO phonon interaction (\( \tau_{eh-LO} \)) can be derived (equation 6.3). This lifetime is referred to as \( \tau^* \) by Ridley (1991).

\[ \tau_{eh-LO} = \frac{-\hbar \omega_{LO}}{k \frac{dT_{eh}}{d\tau}} \cdot \left[ \exp \left( -\frac{\hbar \omega_{LO}}{k T_{eh}} \right) - \exp \left( -\frac{\hbar \omega_{LO}}{k T_{LO}} \right) \right] \]  \hspace{1cm} (6.3)

When a non-equilibrium LO phonon distribution occurs \( T_{LO} \) is a function of time and hence equation 6.3 is bi-exponential. This equation reduces to a single exponential when \( T_{LO} = T_{LA} \)
and is time independent. For this reason bi-exponential cooling behaviour is evidence of a hot phonon effect.

Equation 6.3 has two unknown parameters: $T_{LO}$ and $\tau_{eh-LO}$. In figure 6.13 values of $T_{LO}$ calculated for a range of $\tau_{eh-LO}$ values are shown. In samples O1 and I4, $T_{LO}$ rises and then decays back down again. This is a consequence of the bi-exponential cooling behaviour in these samples. Sample O2 only shows exponential cooling behaviour. This might indicate that a hot phonon effect is not taking place in this sample. It is also possible that bi-exponential behaviour occurs in the 750 ps between the start of the pulse and time zero, such that the $T_{LO}$ population is already hot at time zero. A shorter pulse length would be required to interrogate this time regime.

It can be assumed that $T_{LO} > T_L$ and hence substituting $T_{LO} = T_L$ into equation 6.3 provides a maximum possible value for $\tau_{eh-LO}$. For sample O1 the maximum value of $\tau_{eh-LO}$ was calculated to be 20 ps. This value corresponds to the LO phonon population heating beyond 500 K above that of the surrounding lattice (Figure 6.13). For lower values of $\tau_{eh-LO}$, the temperature gradient between the LO phonons and the surrounding lattice will be even greater. In sample I4 $\tau_{eh-LO} < 40$ ps is required, which produces $T_{LO} - T_L > 200$ K.
Figure 6.13: Values of $T_{LO}$ are calculated for a range of $\tau_{eh-LO}$ values and compared with $\Delta T$, as a function of time. Top: sample O1. Mid: sample O2. Bottom: sample I4.
Conclusions and future perspectives

This study examined intrinsic loss mechanisms which lead to an efficiency limit for solar energy conversion. Five intrinsic loss mechanisms were identified and quantified: thermalisation loss, below $E_g$ loss, emission loss, Carnot loss and Boltzmann loss. Thermalisation loss, below $E_g$ loss and Boltzmann loss account for 33%, 25% and 9% of the total incident solar spectrum at the optimal single junction bandgap and hence these losses must be targeted in novel device designs to obtain substantial efficiency enhancement. In an HCSC, thermalisation loss is directly targeted. Below $E_g$ loss is indirectly targeted because low bandgap materials are optimal for hot carrier absorbers. Boltzmann loss might also be mitigated because the requirement for high carrier density means that HCSCs are likely to be CPV devices.

A hot carrier solar cell is formed of an absorber, which maintains a steady-state non-equilibrium carrier distribution and energy selective contacts, which enable isoentropic carrier thermalisation. The primary focus of this study was to evaluate the suitability of strain-balanced InGaAs/GaAsP QW structures as hot carrier absorbers, using a range of spectroscopic tech-
niques. Previous studies had shown that QW structures exhibited slow carrier cooling rates however, many of the systems investigated suffered from material defects such as aluminium oxidisation and lattice mismatch. The strain-balanced InGaAs/GaAsP QW structure can be grown with excellent material quality making it a candidate for developing high efficiency devices. There are no other published studies of hot carrier effects in InGaAs/GaAsP QW structures.

In this study samples were characterised extensively using CWPL to determine carrier concentration regimes where the steady-state carrier distribution temperature was hotter than that of the surrounding lattice and to identify parameters of the QW structures which enhanced this effect. It was found that deep, wide wells produced the hottest carriers, with a value of $\Delta T = 150$ K measured at an incident carrier concentration of $\sim 1000 \text{ W} \cdot \text{cm}^{-3}$, which is equivalent to approximately 10,000 Suns concentration.

High energy tail fitting was used to quantify carrier distribution temperature. A density dependent PLE set-up was designed and assembled in order to test the validity of the method. It was confirmed that exciton bleaching induced at high carrier concentration did not significantly alter the shape of the absorption profile. The absorption coefficient could therefore be assumed to vary slowly compared with the exponential behaviour of the Fermi function, permitting the use of high energy tail fitting.

The absolute value of absorption coefficient, below the bandgap of the GaAs buffer and substrate could be determined using transmission spectroscopy. By photo-exciting carriers directly into the well region of the samples using a 920 nm laser wavelength and using the experimentally determined absorption coefficient values, $\Delta T$ could be measured as a function of absorbed power density. It was found that the single well sample I1 produced hotter carriers at lower absorbed carrier densities than the matching MQW sample I4. This is because the exponential behaviour of Beer’s law results in high absorption of photons in the first QW and progressively less absorption in subsequent wells. This same feature is reflected in the calculations of thermalisation coefficient, were the single QW sample produced a Q value of $9.53 \pm 0.63 \text{ W} \cdot \text{K}^{-1} \cdot \text{cm}^{-2}$ whereas the 10 well sample produced a Q value of $230.41 \pm 13.68 \text{ W} \cdot \text{K}^{-1} \cdot \text{cm}^{-2}$. The lower the thermalisation coefficient, the slower the energy loss rate.
Large optical path length is required for high energy conversion efficiency and hence simply using narrow absorbers to generate high volumetric carrier density is not a practical solution for a real world HCSC. It might be possible to produce high volumetric carrier density in single QW structures by exploiting strong absorption in the bulk buffer region surrounding a QW and subsequent carrier capture into the well. In addition, nanophotonic structures such as back surface DBRs or front surface scattering structures might be implemented to produce high carrier density.

Previous studies have shown that a thermalisation coefficient equal to or less than $10 \text{ W} \cdot \text{K}^{-1} \cdot \text{cm}^{-2}$ is required to generate a hot carrier solar energy conversion efficiency enhancement in a device under 10,000 Suns concentration. The thermalisation coefficient was calculated to be $20.06 \pm 0.85 \text{ W} \cdot \text{K}^{-1} \cdot \text{cm}^{-2}$ in MQW sample O1. This structure has a long optical path length at 920 nm but still produces a low thermalisation coefficient. Reducing the number of wells in this sample from 10 to 5 and introducing a DBR on the back surface window layer of the structure should allow the target value of $10 \text{ W} \cdot \text{K}^{-1} \cdot \text{cm}^{-2}$ to be easily achieved in this sample structure, while maintaining an equivalent photon absorption per unit area.

TRPL spectroscopy was used in this study to provide insight into hot carrier dynamics in the strain-balanced InGaAs/GaAsP QW material system. In the first instance, upconversion spectroscopy was performed on sample I4 at the University of Sydney. Hot carriers were observed beyond 2 ns after photo-excitation. The carrier cooling behaviour was well described by a bi-exponential function suggesting two different mechanisms were contributing to carrier cooling. This might be the result of a hot phonon effect. Initially after photo-excitation, energy is rapidly transferred from the carrier distribution to LO phonons. The LO phonons are unable to dissipate the energy as LA phonons fast enough to maintain equilibrium and hence the LO phonon population heats up, slowing the rate of energy transfer from carriers to LO phonons.

Streak camera TRPL was used to characterise samples O1, O2 and I4 with a 920 nm photo-excitation wavelength, for a range of carrier densities. As with CWPL, it was found that sample O1 produced the hottest carriers with $\Delta T = 2000 \text{ K}$ recorded at times $< 5 \text{ ns}$ for well
region carrier density $\sim 1 \times 10^{17} \text{ cm}^{-3}$. No hot carriers were observed at anytime with low carrier densities ($\sim 3 \times 10^{15} \text{ cm}^{-3}$). It was determined that the low number of counts available per spectrum produced large uncertainties in the calculated values of carrier distribution temperatures and hence it was not possible to use this data to develop further understanding of the underlying mechanisms which induce hot carrier behaviour. With much longer acquisition times, signal to noise, and hence the quality of the high energy tail fitting could be improved.

TCSPC was used to characterise samples O1, O2 and I4. Long acquisition times were used to provide a large number of counts over the 3D parameter space. It was shown that in samples O1 and O2 cooling lifetimes ($\tau_{th}$) were very similar at low $\Delta T$ values. These samples have different well widths and hence have very different electronic dispersion, however, they have the same atomic composition and consequently have almost identical phononic dispersion. It is possible that carrier cooling in the low $\Delta T$ regime, in which samples O1 and O2 show very similar behaviour, is dominated by LO-LA phonon scattering. This is a purely phononic cooling pathway and hence would not be altered by the different electronic dispersion of the two samples. Sample I4 has different atomic composition and also exhibits shorter carrier cooling lifetimes than samples O1 and O2 in the low $\Delta T$ regime.

Samples O1 and I4 also exhibit a high $\Delta T$ cooling behaviour, characterised by much shorter carrier cooling lifetimes. This bi-exponential carrier cooling behaviour was also observed in the upconversion spectroscopy and might be attributed to a hot phonon effect. Using the Ridley (1991) formalism and assuming the rate of carrier-LO phonon interaction is constant, it was found that bi-exponential carrier cooling behaviour is characteristic of a hot LO phonon population. The absence of this behaviour in sample O2 does not necessarily preclude a hot phonon effect. LO phonon heating and hence bi-exponential carrier cooling in sample O2 might be occurring before the end of the excitation pulse and hence cannot be observed.

Maximum values of carrier-LO phonon interaction lifetimes were calculated to be 20 ps and 40 ps for samples O1 and I4 respectively. Given these maximum lifetimes, the LO phonon distributions must reach temperatures of at least 500 K and 200 K above that of the surrounding lattice for samples O1 and I4 respectively.
7.1 Future perspectives

This study has been successful in demonstrating hot carrier effects in the strain-balanced InGaAs/GaAs QW material system and giving insight into the physical mechanisms which cause these effects, providing a guide to developing the first proof of concept hot carrier device. The next step for this project will be to measure a hot carrier photocurrent in a real device, designed using the knowledge that has been acquired on hot carrier absorber materials and energy selective contacts. In the first instance, this could be achieved by growing a p-i-n structure with a single deep, wide well in the intrinsic region. Quasi energy selective contacts are formed by the well region barriers. Thermalisation occurring in the barriers will be partly entropic because the energy selectivity is step like rather than narrow band. Any drop in energy bandgap beyond the barrier will result in further entropy generation, hence the GaAs buffer layer should be completely removed if possible. The presence of the buffer region would result in a reduction in optimal operating voltage and hence a reduction in device efficiency.

In addition, further characterisation of these structures might allow a full understanding of cooling pathways and associated rates to be established for this material system. TRPL measurements using a spectroscopic set-up similar to the streak camera system used in Kobe (section 4.5.2) would allow carrier-LO phonon cooling lifetime ($\tau_{eh-LO}$) to be definitively determined. The TCSPC system only allows maximum values of $\tau_{eh-LO}$ to be determined because of the long pulse duration. In order to obtain the desired low levels of uncertainty on carrier distribution temperature, much longer acquisition times than those used in the previous streak camera measurements would be required. Also, a smaller spot size would be necessary to explore higher carrier density regimes.

Time resolved Raman spectroscopy is a characterisation technique in which LO-LA cooling lifetime ($\tau_{LO-LA}$) can be determined. The sample is illuminated with laser light and this is scattered by phonon interactions. Scattered laser light is therefore shifted by the energy of a phonon. The returning scattered light is detected as a function of time and spectrally analysed allowing LO-LA cooling lifetime to be determined by comparing the intensity of the Raman peaks. With a measured value of $\tau_{LO-LA}$, carrier cooling pathways could be fully characterised.
7.1 Future perspectives

using the energy balance rate model described in section 3.6. Such a comprehensive model of carrier dynamics would be invaluable in further HCSC absorber structure optimisation.
Appendices
A Generalised Planck derivation

The generalised Planck equation is derived by considering the density of photon states in the body \(dN_{ph}(E)/dE\) and the probability that those states are occupied \((f_{ph}(E,T))\). A geometrical factor is also required to describe the angular emission out of the surface of the body (De Vos, 2008).

A.1 Density of photon states

The density of photon states \(D_{ph}(E)\) can be derived from the uncertainty principle, analogously to \(D_e(E)\). The number of electron states \(N_{ph}(p)\) in a unit sphere in phase space is the same as for electron states, equation A.1.

\[
N_{ph}(p) = N_e(p)
\]  
(A.1)
Photon energy and momentum are related by the expression shown in equation A.2, allowing conversion between momentum and energy space.

\[ E = pc \]  

(A.2)

Equation A.2 is substituted into equation 1.10 to give the number of photon states with energy less than \( E \) in volume \( V \), Equation A.3.

\[ N_{ph}(E) = 2 \left( \frac{4\pi E^3}{c^3} \right) \frac{8\pi E^3 V}{3c^3h^3} \]  

(A.3)

The density of photon states per unit energy is found by taking the derivative of \( N_{ph}(E) \), with respect to energy, equation A.4.

\[ \frac{dN_{ph}(E)}{dE} = \frac{8\pi E^2 V}{c^3h^3} \]  

(A.4)

**A.2 Geometrical factor**

Black and grey bodies are isotropic emitters however, often only a limited range of emission angles will be relevant to a calculation. In the case of solar radiation, only light emitted out of the surface of the Sun into a small cone subtended by the solar disk will reach a solar cell on the surface of the earth. A further geometrical factor is required to calculate the photon flux escaping the surface of the body into the relevant angular range.

The solid angle of a sphere in steradians (sr) is \( 4\pi \) and therefore the fraction of total radiation emitted from a body into solid angle \( d\omega \) is given by \( d\omega/4\pi \). Photons will travel a distance \( c\,dt \) in a time interval \( dt \), where \( c \) is the speed of light in a vacuum. Photons emitted at angle \( \theta \) to the normal, from surface element \( dS \) will have been generated in volume \( V = c\,dt\cos\theta\,dS \) of the body, figure A.1.

Substituting this value of \( V \) into equation A.4 and multiplying by \( d\omega/4\pi \) will give an expression for the density of photon states per unit energy interval, emitted through surface element \( dS \),
A.3 Occupation of photon states

Photons emitted through a surface $dS$, in time $dt$, at angle $\theta$ to the normal of the surface, originating from black body volume $V = c \, dt \cos \theta \, dS$.

$$\text{Figure A.1:} \text{ Photons emitted through a surface } dS, \text{ in time } dt, \text{ at angle } \theta \text{ to the normal of the surface, originating from black body volume } V = c \, dt \cos \theta \, dS.$$ 

into solid angle $d\omega$, in time interval $dt$ (equation A.5)

$$\frac{dN_{ph}(E, \omega)}{dE} = \frac{8\pi E^2}{c^3 h^3} \cdot c \, dt \cos \theta \, dS \cdot \frac{d\omega}{4\pi} = \frac{2E^2}{c^2 h^3} \cos \theta \, d\omega \, dS \, dt$$

Integrating over the relevant solid angle and taking $dt = dS = 1$ gives an expression for the flux of photon states emitted from a body per unit surface area, per unit energy interval, equation A.6

$$D_{ph}(E, \Omega) = \frac{2\Omega}{c^2 h^3} E^2$$

Emission into a hemisphere is described by $\Omega_{\text{hemi}} = \pi$. This can be used to described emission from a solar cell. The solid angle subtended by the Sun is given by $\Omega_S = 6.8 \times 10^{-5}$.

A.3 Occupation of photon states

Photons are bosons and therefore their distribution is described by Bose-Einstein statistics. The Bose-Einstein distribution, equation A.7, gives the probability of a photon state being occupied. $T$ is the temperature of the emitting body and $k$ is Boltzmann’s constant.

$$f_{ph}(E, T) = \frac{1}{\exp[E/kT] - 1}$$

The occupation of photon states in a population with non-zero chemical potential ($f_{ph}(E, T, \mu)$)
A.3 Occupation of photon states

is calculated by considering generation and recombination mechanisms occurring in the emitting body (Fox, 2001). Equation A.8 shows the probability \( R \) with which any radiative process occurs. This is the sum of the probabilities of each individual radiative process, shown in figure 1.12.

\[
R = f_{ph}f_1(1 - f_2) + f_{ph}f_2(1 - f_1) + f_2(1 - f_1)
\]  

(A.8)

The rate of change in \( f_{ph}(E, T, \mu) \) resulting from radiative generation and recombination mechanisms is given by equation A.9, where \( (C) \) is a constant scaling factor. When temperature and chemical potential are constant, the photon population forms a steady state and hence this rate of change is zero.

\[
\frac{df_{ph}(E, T, \mu)}{dt} = CR = 0
\]  

(A.9)

An expression for photon occupation probability in a body with non zero chemical potential follows, equation A.10.

\[
f_{ph}(E, T, \mu) = \frac{1}{f_2(1 - f_2) - 1} - 1
\]

\[
= \frac{1}{\exp\left(\frac{E - \mu}{kT}\right) - 1}
\]

(A.10)

Electron and hole occupation probabilities, \( f_2 \) and \( f_1 \), are described by equations 1.14 and 1.15 respectively.

The photon flux \( (n_{ph}(E, T, \mu, \Omega)) \) emitted from a black or grey body per unit energy interval is the product of available photon states, equation A.6, the probability of their occupation, equation A.10, and the emissivity of the material, \( \epsilon(E) \). This is the generalised Planck equation (Equation A.11).

\[
n_{ph}(E, T, \mu, \Omega) = \epsilon(E) \frac{2\Omega}{c^2h^3} \frac{E^2}{\exp[(E - \mu)/kT] - 1}
\]

(A.11)
Sample structures

<table>
<thead>
<tr>
<th>layer</th>
<th>material</th>
<th>width (nm)</th>
<th>repeats</th>
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<td>window</td>
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**I1 : single shallow well**

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<tr>
<td>well</td>
<td>In$<em>{0.11}$Ga$</em>{0.89}$As</td>
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**I2 : 10 shallow wells**

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O1: 10 deep, wide wells

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O2: 20 deep, narrow wells

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References


REFERENCES

M. A. Green. *Third generation photovoltaics: advanced solar energy conversion*. Springer, 2006. 61, 64


REFERENCES


