1 Theory

1.1 Light absorption and carrier creation in GaAssolar cells

1.2 Carrier recombination in GaAssolar cells

Once an electron-hole pair has been created by the absorption of a photon, there are two major possibilities for its development: either the pair is successfully separated by the junction, traverses an external circuit and is active in providing energy, or the electron-hole pair can recombine. Recombination can either be radiative or non-radiative. In radiative recombination, a photon of corresponding energy is released, whereas in non-radiative recombination, either a phonon is released (Shockley-Read-Hall recombination) or the excess energy is passed on to a third carrier (Auger recombination).

- Charge collection
- Recombination
  - Radiative Recombination
  - Non-Radiative Recombination
    - Shockley-Read-Hall recombination
    - Auger recombination

In solar cells, non-radiative recombination is an unwanted phenomenon since it constitutes loss of generated carriers and thus loss of energy. Auger recombination is a minor issue in III-Vsolar cells: it is a three body collision process and thus intrinsically improbable to happen. Non-radiative recombination at trap-states within the energy-gap is, however, still a major concern. Such trap-states can be created by imperfections in the crystal lattice, crystal-defects or impurities. With current high-quality GaAsgrowth techniques, impurities are of less concern than imperfections. An 'ideal' crystal is a purely theoretical construct: its translation symmetry is never broken, thus the 'ideal' crystal has to be infinite. Consequently, in a real crystal, even in a perfectly pure one, surfaces constitute imperfections since the crystal symmetries are broken here. To avoid loss of energy through recombination at the back side of the solar cell, a so called 'back surface field' (BSF) can be included in the cell during growth. It induces an electrical field to 'push' minority carriers away from the surface, back into the bulk again. Similar strategies exist for the front surface.

1.3 Side-surfaces

Because solar-cells are grown layer by layer parrallel to the front and back surface, each individual layer being homogenous, it is not possible to employ a strategy similar to the BSF to avoid carrier recombination at the side surfaces of solar cells. As a rough estimate, a typical GaAssolar cell grown in the laboratory for research purposes has sides on the order of centi-meters and thickness on the order of micro-meters. Thus, a cell's side-surface is $\sim \frac{1}{10000}$ the size of its front or back surface. Whatever the precise dimensions may be, the side-surfaces are much smaller than front- and back surfaces, still research has shown that their influence on dark-currents in the cell is of great importance.

1.4 Rau's reciprocity relation

In 2007, Rau published a paper with interesting reciprocity relations relating electrical properties of a solar cell to optical properties of the same device operated as a LED. It will become clear that from a simple, standardised measurement of the external-quantum-efficiency (EQE) of a solar cell, a wealth of information can be gained. A mathematically rigorous derivation is provided by Rau, relying on a more fundamental theorem by Donolato. However, in the following, we will chose an intuitive approach to obtain the same results because they implications of the formulæthus derived will become clear more easily. The interested reader is referred to the original publication for the more mathematical approach.

We start with Planck's radiation law in its most well-known form:

$$B_\lambda(T) = \int_{\lambda_1}^{\lambda 2} \frac{2\,\pi\,h\,c^2}{\lambda^5} \frac{d\lambda}{\exp(\frac{hc}{\lambda kT}) - 1}\,, \tag{1}$$

where h is Planck's constant, c the speed of light, k the Boltzmann constant and T the absolute temperature. $B_\lambda(T)$ gives the energy density of a black-body at temperature T in terms of the wavelength, but we are more interested in the corresponding flux density: Using

$$E(\lambda) = \frac{hc}{\lambda} \tag{2}$$

the spectral photon density becomes

$$\Phi_\lambda(T) = \int_{\lambda_1}^{\lambda 2} \frac{2\,\pi\,c}{\lambda^4} \frac{d\lambda}{\exp(\frac{hc}{\lambda kT}) - 1}\,. \tag{3}$$

The derivative of (2) is:

$$\frac{dE}{d\lambda} = -\frac{hc}{\lambda^2}\,. \tag{4}$$

So:

$$\Phi_\lambda(T) = \int_{\lambda_1}^{\lambda_2} \frac{2\,\pi\,c}{\lambda^4} \frac{d\lambda}{\exp(\frac{hc}{\lambda kT}) - 1} \tag{5}$$

$$\Phi_E(T) = \int_{E(\lambda_2)}^{E(\lambda_1)} \frac{2\,\pi}{h\,\lambda^2} \frac{dE}{\exp(\frac{hc}{\lambda kT}) - 1} \tag{6}$$

$$= \int_{E(\lambda_2)}^{E(\lambda_1)} \frac{2\,\pi}{h^3\,c^2} \frac{E^2\,dE}{\exp(\frac{E}{kT}) - 1}\,, \tag{7}$$

which means that in thermal equilibrium, each surface element of a solar cell is irradiated from each element of the spherical angle θ of the ambient with a spectral flux density:

$$\phi_{eq}(E_\lambda, T, \theta) = \phi_{E_\lambda}(T) cos(\theta) \tag{8}$$

$$= \frac{2}{h^3\,c^2} \frac{E_\lambda^2\,\cos(\theta)}{\exp(\frac{E_\lambda}{kT}) - 1} \tag{9}$$

$$\approx \frac{2E_\lambda^2\,\cos(\theta)}{h^3\,c^2} \exp(\frac{-E_\lambda}{kT})\,, \tag{10}$$

where E_λ is the energy of photons of wavelength λ. The last approximation can be used to obtain analytical solutions if all spectra are taken as black-body radiation functions. However, since it is more common in the field of solar cells to use the AM1.5 reference spectrum, we will use the exact formulation and obtain numerical results.
A portion $\alpha(r_S, \theta, \varphi, E_\lambda)$ of that radiation will be absorbed by the solar cell, depending on the coordinate r_S of the surface element dS of the cell and the angles of incidence θ & φ. Accordingly, the probability that one photon impinging on the cell will contribute one elementary charge q to the short-circuit current of the cell will be given by $Q(r_S, \theta, \varphi, E_\lambda) = \alpha F_C$, where F_C is the probability

for a charge carrier to be collected by the junction [1]. Thus, from thermal radiation, there will be a short-circuit current component

$$J_{SC,0} = q \int_{\Omega_c} \int_{E_\lambda} \int_{S_C} Q(r_S, \theta, \varphi, E_\lambda) \phi_{eq}(\theta, E_\lambda) d\Omega dE_\lambda dS \,, \tag{11}$$

which will be called the dark-equilibrium-short-circuit current. The integral extends over the full spherical angle $\Omega_c = 2\pi$. Because of thermal equilibrium, no net current will be flowing, so we can postulate that $J_{SC,0}$ will be counterbalanced by an equilibrium injection current $J_{em,0} = J_{SC,0}$ for which the relation

$$\delta J_{em,0} = \delta J_{SC,0} = qQ\phi_{eq} \tag{12}$$

also holds throughout the entire cell. Thus, it can be seen that in thermal equilibrium, light injection with *subsequent carrier collection* is precisely counter-balanced by current injection with *subsequent light emission.*

However, under illumination from the sun, an excess flux density ϕ_{sun} impinges on the cell, so the short-circuit current will be given by

$$J_{SC} = q \int_{\Omega_{sun}} \int_{E_\lambda} \int_{S_C} Q(r_S, \theta, \varphi, E_\lambda) \phi_{sun}(\theta, \varphi, E_\lambda) d\Omega dE_\lambda dS \,. \tag{13}$$

Rau proceeded to postulate that the injection current δJ_{em} under an applied bias voltage would follow an exponential law and that it were superimposed on the dark-equilibrium-short-circuit current, so that the excess photon flux density ϕ_{em} emitted from the device would follow Shockley's diode law:

$$\phi_{em}(r_S, \theta, \varphi, E_\lambda) = Q(r_S, \theta, \varphi, E_\lambda) \phi_{eq}(\theta, E_\lambda) (\exp(\frac{qV}{kT}) - 1) \,. \tag{14}$$

Thus, from a known Q – i.e. EQE – the spectral and angular emmittance of the device if operated as a LED can be calculated. The derivation is strictly valid only for angular EQE measurements, but Green has shown that deviations from the exact results are small enough to allow an approximation of the method by measuring just the perpendicular component of the EQE.

Furthermore, through the relation $V_{OC} = kT/q \ln(J_{SC}/J_0 + 1)$ we can calculate a maximum attainable open-circuit voltage for a given device, once we realise that the minimum recombination current will be given by the equilibrium injection current:

$$V_{OC}^{rad} = \frac{kT}{q} \ln(\frac{J_{SC}}{J_{em,0}} + 1) \,. \tag{15}$$

This maximum open circuit voltage is in a sense more realistic than Shockley and Queisser's limit in that it takes into account the devices actual quantum efficiency and does not model the absorption as a step function $\alpha(E_\lambda) = 1$ for $E_\lambda > E_g$ and $\alpha(E_\lambda) = 0$ for $E < E_g$. Equation (15) can be seen as the most important result of this derivation, since it will allow us to compare the performance of solar cells based on their maximum attainable open-circuit voltage, *the* parameter which has to be improved upon to achieve another world-record solar cell at AMS.

[1] in the field of photo-voltaics, the quantity Q is known as the external-quantum-efficiency of a solar cell