## Limits on light emission from silicon

Invited Paper Peter Würfel

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Although silicon is an indirect semiconductor, light emission from silicon is governed by the same generalized Planck's radiation law as the emission from direct semiconductors. The emission intensity is given by the absorptance of the volume in which there is a difference of the quasi Fermi energies. A difference of the Fermi energies may result from the absorption of external light (photoluminescence) or from the injection of electrons and holes via selective contacts (electroluminescence). The quantum efficiency may be larger than 0.5 for carrier densities below  $10^{15}$  cm<sup>-3</sup>. At larger densities, non-radiative recombination, in particular Auger recombination dominates. At all carrier densities, the relation between emission intensity and difference of the quasi Fermi energies is maintained. Since this difference is equal to the voltage of a properly designed solar cell, luminescence is the key indicator of material quality for solar cells.

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Light emission from semiconductors is governed by Planck's radiation law after generalizing to emitters with a non-zero difference of the quasi Fermi energies  $\varepsilon_{\rm FC} - \varepsilon_{\rm FV}$  for the conduction and the valence bands<sup>[1]</sup>. The spontaneous emission rate of photons with energy  $\hbar\omega$  is

$$dr_{\rm sp}(\hbar\omega) = \alpha_{\rm bb}(\hbar\omega) \frac{4\pi n^2}{4\pi^3 \hbar^3 c_0^2} \frac{(\hbar\omega)^2}{\exp\left[\frac{\hbar\omega - (\varepsilon_{\rm FC} - \varepsilon_{\rm FV})}{kT}\right] - 1} d\hbar\omega, \quad (1)$$

where  $\alpha_{\rm bb}(\hbar\omega)$  is the absorption coefficient for bandband transition, n is the refractive index of the emitting material,  $c_0$  is the velocity of light in vacuum, K is the Boltzmann constant, and T is the absolute temperature. The difference of the quasi Fermi energies, which characterize two different Fermi distributions, separately describing the occupation of the conduction band and the valence band, is equal to the chemical potential  $\mu_{\gamma}$  of the emitted photons.

For indirect transitions as in silicon, it is not immediately obvious that the photon emission rate is proportional to the coefficient  $\alpha_{\rm bb}(\hbar\omega)$  as stated by Eq. (1). The reason is as follows. Consider an absorption event at  $\hbar \omega > \varepsilon_{\rm G}$ , the band gap of the semiconductor, in which a photon is absorbed and a phonon is emitted in an indirect transition. The phonon emission is not restricted and equally possible at any temperature. The probability of this process defines the absorption coefficient  $\alpha_{\rm bb}(\hbar\omega)$ . If this process is reversed to emit a photon of the same energy  $\hbar\omega$ , a phonon must be absorbed, when the electron-hole pair recombines. The probability for this process is proportional to the phonon density and, therefore, depends on the temperature. It is quite unexpected that the emission of a photon together with the absorption of a phonon should be proportional to the absorption coefficient, which is measured for the absorption of a photon together with the emission of a phonon. However, a somewhat detailed analysis<sup>[2]</sup> shows that Eq. (1) is indeed valid for indirect transitions as well, provided that the phonons are in thermal equilibrium and have a chemical potential  $\mu_{\Gamma} = 0$ , a condition which is hard to violate considering the short lifetime of the phonons.

The rate in Eq.(1), at which photons are emitted inside a material, cannot be observed. What can be observed is the photon current emitted from the surface of a semiconductor body and this depends on its geometry. For the absorption of incident light, the geometry of the absorbing body is contained in its absorptance a, which for the simple case of a homogeneous plate with thickness dis

$$a(\hbar\omega) = [1 - r(\hbar\omega)] \{1 - \exp\left[-\alpha(\hbar\omega)d\right]\},\qquad(2)$$

where  $r(\hbar\omega)$  is the reflectance. An equivalent result follows from integrating the rate  $dr_{\rm sp}$  in Eq. (1) over the thickness of the sample and considering reabsorption. The photon current density emitted through the surface of a homogeneously excited plate into a half space in vacuum is

$$j_{\gamma} = \int_{0}^{\infty} \frac{a(\hbar\omega)}{\alpha_{\rm bb}(\hbar\omega) 4n^2} \mathrm{d}r_{\rm sp}.$$
 (3)

The factor of  $4n^2$  in the denominator is caused by the density of states for photons, which is smaller in vacuum by  $n^2$  than in the semiconductor and by Lambert's law, which reduces the effective solid angle from  $4\pi$  for isotropic emission to  $\pi$  for emission from a plane surface into a half space. As a result, many photons emitted in the bulk towards the surface will experience total internal reflection.

For a silicon light emitting diode (LED), an external quantum efficiency a little over 1% has been observed in electro luminescence<sup>[3]</sup>. An even larger efficiency a little over 6% was observed for a Si wafer without contacts in photo luminescence<sup>[4]</sup>. It is, however, not clear from

these experiments at what intensities these efficiencies have been observed and if they warrant hope for silicon as an efficient light source. We discuss this question in the following for a device in the geometry of a plate of thickness d. One large surface, through which the photons are emitted, has an ideal antireflection coating resulting in zero reflectivity, while ideal mirrors cover all other surfaces. The electrodes by which electrons and holes are injected into the bulk of the device are carrier selective. One contact shall exchange only electrons and the other contact shall exchange only holes when a voltage V is applied. Because of the assumed large diffusion lengths for both charge carriers, an applied voltage Vcauses a homogeneous difference of the Fermi energies of  $\varepsilon_{\rm FC} - \varepsilon_{\rm FV} = eV$  inside the device with e being the elementary charge.

The emission spectrum of silicon at room temperature is narrow and centered at the band gap energy  $\varepsilon_{\rm G}$ . In this photon energy range, the absorption coefficient of silicon is rather small. Literature data<sup>[5]</sup> weighted according to Eq. (1) result in an average value of the absorption coefficient of Si of only  $0.2 \text{ cm}^{-1}$  over the emission spectrum. Even for the  $300-\mu m$  thickness of a typical silicon wafer with an ideal antireflection coating, the absorptance averaged over the emission spectrum is only 0.006 for a single pass. This is one of the reasons why we do not yet have silicon LEDs. The other reason is non-radiative recombination. There are two major processes, recombination via impurities and defects, and Auger recombination. While the first process is eliminated in pure single crystal silicon, Auger recombination is of a fundamental nature. In an Auger process, an electron and a hole recombine and give their energy to another free electron or hole which is excited high into its respective band, but looses its large kinetic energy quickly by phonon scattering. The Auger recombination rate is

$$R_{\rm Aug} = \left(C_{\rm e}n_{\rm e} + C_{\rm h}n_{\rm h}\right)n_{\rm e}n_{\rm h}.\tag{4}$$

For silicon, the Auger coefficients are  $C_{\rm e} \approx C_{\rm h} \approx 10^{-30} \text{ cm}^6/\text{s}$ . For a given difference of the quasi Fermi energies, the product of the carrier densities is

$$n_{\rm e}n_{\rm h} = n_{\rm i}^2 \exp\left[\frac{\varepsilon_{\rm FC} - \varepsilon_{\rm FV}}{kT}\right] \tag{5}$$

with the intrinsic carrier concentration in silicon  $n_i = 10^{10} \text{ cm}^{-3}$ . For a given difference of the Fermi energies, i.e., for a given voltage and a given emitted intensity, according to Eq. (3), the Auger recombination rate is minimal for  $n_e = n_h$ , i.e., for a doping density smaller than the density of the injected carriers. This case will be considered in the following.

The emission intensity from silicon may be small, but it could still be very efficient, if the rate of radiative recombination is larger than the rate of Auger recombination.

The external quantum efficiency  $\eta_{\gamma}$  is the number of photons emitted through the surface for each electronhole pair in the injected particle current  $j_{\rm eh}$ . This particle current has to compensate the losses due to Auger recombination and due to that part of the radiative recombination which generates photons that do not again generate electron-hole pairs, when they are reabsorbed. These are the photons, which are emitted through the front surface or are absorbed by free carriers or other parasitic absorption processes. In the absorption coefficient  $\alpha(\hbar\omega) = \alpha_{\rm bb}(\hbar\omega) + \alpha_{\rm fc} + \alpha_{\rm ps}$ , we consider the contributions from band-band transitions  $(\alpha_{\rm bb}(\hbar\omega))$ , from free carrier absorption  $(\alpha_{\rm fc} \approx 2.5 \times 10^{-18} \text{ cm}^2 \times n_{\rm e,h})$  and parasitic processes  $(\alpha_{\rm ps})$  which are both assumed to be independent of  $\hbar\omega$  over the range of the emission spectrum. If non-band-band processes are present, the absorptance  $a(\hbar\omega)$  in Eq. (3) has to be replaced by  $a(\hbar\omega) \times \alpha_{\rm bb}(\hbar\omega)/\alpha(\hbar\omega)$ , since only band-band transitions contribute to the emission.

The particle current, which is injected to replace the lost charge carriers, is

$$j_{\rm eh} = j_{\gamma} + d \left( R_{\rm Aug} + \int_{0}^{\infty} \mathrm{d}r_{\rm sp} \frac{\alpha_{\rm ps} + \alpha_{\rm fc}}{\alpha_{\rm bb}} \right).$$
(6)

We can now define the quantum efficiency

$$\eta_{\gamma} = \frac{j_{\gamma}}{j_{\rm eh}},\tag{7}$$

and the energy efficiency

$$\eta_{\rm E} = \frac{j_{\rm E}}{e j_{\rm eh} V},\tag{8}$$

where the emitted energy current density  $j_{\rm E}$  (intensity) follows from Eq. (3) by multiplying the integrand by  $\hbar\omega$ .

Figure 1 shows the results of a computation of the quantum efficiency  $\eta_{\gamma}$  and the energy efficiency  $\eta_{\rm E}$  for a 10- $\mu$ m-thick silicon film with and without absorption by free carriers and other parasitic processes (we assume  $\alpha_{\rm ps} = 0.01 \text{ cm}^{-1}$ ) as a function of the applied voltage V. We see that the quantum efficiency is 100% if there are only band-band transitions and the rate of Auger recombination is small at small voltages. Including only 5% of parasitic absorption and free carrier absorption (negligible at small voltages), however, reduces the quantum efficiency is much larger than



Fig. 1. Quantum efficiency  $\eta_{\gamma}$  and energy efficiency  $\eta_{\rm E}$  for emission from a plane silicon film of 10- $\mu$ m thickness in the presence of Auger recombination with (para) and without parasitic absorption by defects ( $\alpha_{\rm ps} = 0.01 \text{ cm}^{-1}$ ) and free carriers. The emitted intensity (not shown) rises exponentially with the voltage and is 40  $\mu$ W/cm<sup>2</sup> at V = 0.8 V for both cases.

one at small voltages. The energy of the emitted photons is only partly supplied by the voltage source, and the rest comes from heat of the semiconductor, which acts as a heat pump and is cooled by the emission.

The dramatic effect of parasitic absorption can be reduced by increasing the probability for the photons to get out of the semiconductor. This is achieved by light trapping structures, which scatter the photons and enhance the absorptance<sup>[1]</sup>. As long as the absorptance is small, the photon path length can ideally be enhanced to  $4n^2d \approx 48d$  for silicon. Figure 2 shows that this ideal light trapping reduces the effect of parasitic absorption and even of Auger recombination, extending large quantum efficiencies to higher voltages. With ideal light trapping, the ultimate intensity from a thin silicon film is achieved. The emitted energy current density is about  $1 \text{ mW/cm}^2$  at a voltage of 0.8 V. The energy efficiency at this intensity is only about 6%. A higher intensity of  $80 \text{ mW/cm}^2$  is emitted at 0.9 V, however with an energy efficiency of only 0.6%. The intensity can be increased further by increasing the thickness to over 10  $\mu$ m, accompanied by a further reduction in energy efficiency. A larger brightness (energy current density per solid angle) for the same amount of silicon per area may be achieved by an appropriate photonic structure concentrating the light into a smaller solid angle, which would otherwise be emitted into a half space. The ultimate brightness is reached when the absorptance for the emission direction is one.

For larger quantum efficiencies at large intensities, the optical properties of silicon must be improved. Structures on the nanometer scale (e.g., porous silicon), which change the electronic structure, would make silicon a different material with different optical properties. Then even larger efficiencies and emission intensities are imaginable.

Solar cells produce electrical energy from solar heat. This is the task of a heat engine. This task is performed in two steps. The first step is the conversion of solar heat into chemical energy of the electron-hole



Fig. 2. Limiting values of quantum efficiency  $\eta_{\gamma}$  and energy efficiency  $\eta_{\rm E}$  for ideal light trapping in a 10- $\mu$ m-thick silicon film in the presence of parasitic absorption and Auger recombination as in Fig. 1. The emitted intensity  $j_{\rm E}$  is shown in mW/cm<sup>2</sup>.

pairs. This is achieved by cooling the initially hot charge carrier distribution down to room temperature at constant carrier density. This establishes two separate Fermi distributions for the conduction and the valence bands with Fermi energies  $\varepsilon_{\rm FC}$  and  $\varepsilon_{\rm FV}$ . The difference of these Fermi energies is the chemical energy per electron-hole pair obtained from absorbing solar photons. The conversion of solar heat into chemical energy does not need a solar cell, and it occurs in every illuminated semiconductor. The second step is the conversion of chemical energy into electrical energy. It requires the structure of a solar cell, which allows the exchange of electrons only through one contact and of holes only through the other contact and can be 100% efficient. Since the first step is limiting the efficiency, Eq. (3) is so important for solar cell materials and solar cells, because it allows to measure the chemical energy of the electron-hole pairs by quantifying the luminescence. Photo luminescence and electro luminescence compliment each other. Key parameters of solar cell materials such as the lifetime of the minority carriers<sup>[6]</sup> or their diffusion length<sup>[7]</sup> can be determined and using a camera for the detection of the luminescence, high spatial resolution is achieved in imaging the surface of a solar cell.

In conclusion, due to its small absorption coefficient over its emission spectrum, silicon is a poor light emitter. The emission can be enhanced considerably by applying light trapping structures. High quantum and energy efficiencies can be achieved but only for low intensities. At higher intensities, requiring higher concentrations of electron-hole pairs, Auger recombination dominates over radiative recombination, resulting in small quantum and energy efficiencies. Light emission from silicon is, however, a very important tool to characterize the material quality for the application to solar cells. Modern Si complementary metal oxide semiconductor (Si-CMOS) cameras can offer high spatial resolution and short measuring time.

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