Injection dependence of spontaneous radiative recombination in crystalline silicon: Experimental verification and theoretical analysis

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The radiative recombination coefficient B in crystalline bulk silicon is enhanced by the Coulomb attraction between electrons and holes. This effect is weakened at high carrier densities due to screening. We measure the resulting dependence of B on the free-carrier density (i) by reinterpreting published data and (ii) with photoluminescence and photovoltaic measurements. We calculate the Coulomb enhancement by determining the electron-hole pair correlation function at zero interparticle distance, assuming a Debye interaction potential. Both bound and scattering state contributions are fully taken into account. Due to screening, B decreases with increasing free-carrier density. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2218041]

The quantification of the radiative recombination rate in crystalline silicon is important to the present development of efficient light-emitting devices based on this material. Such devices have reached external quantum efficiencies of near 1% for electroluminescence[1] and over 10% for photoluminescence (PL).[2] This is high considering that silicon has an indirect band gap and also influences the performance of solar cells that operate under concentrated sunlight. The rate R of spontaneous radiative recombination is proportional to the density of free electrons n and free holes p. Considering only excess carriers, there holds

$$R = B(np - n_{i,\text{eff}}^2), \tag{1}$$

where B is the radiative recombination coefficient and $n_{i,\text{eff}}$ is the effective intrinsic carrier density. It has been known since 1974 that B is enhanced by the Coulomb attraction between electrons and holes,[3] which leads to an increased hole density in the vicinity of an electron, and vice versa. This enhancement depends on the amount of screening among the free carriers: if there is a sufficient density of free electrons between the mentioned electron and its surrounding holes, their Coulomb attraction is screened. Screening depends on both temperature[3] and carrier injection level.[4] The temperature dependence of B has been thoroughly examined,[3,5–7] while no quantification of the injection dependence is currently available, although it is the dominant effect in light-emitting devices operated at constant ambient temperature. In this letter, we present both measurements and theoretical calculations of the injection dependence.

B can be determined experimentally using two different approaches. First, by measuring R and the density of excess carriers;[3] second, by measuring the absorption coefficient for band-to-band transitions α_{bb} and by applying the van Roosbroeck theory[8] or the generalized Planck equation,[7,9]

$$B = \frac{1}{n_{i,\text{eff}}^2 \pi^2 \hbar^3 c_0^2} \int_0^\infty N^2 E_{\text{ph}}^2 \alpha_{\text{bb}} e^{-E_{\text{ph}}/kT} dE_{\text{ph}}. \tag{2}$$

This formula involves the index of refraction N, the speed of light in vacuum c_0, and the photon energy E_{ph}.

We scale B to B/B_{low}, where B_{low} is obtained at very low carrier densities. We do this because, in contrast to measurements of B, B/B_{low} does not require absolute measurements of the emitted photon flux j_γ; neither are light-trapping and reabsorption processes nor the exact value of $n_{i,\text{eff}}$ involved. Furthermore, calculations relative to B_{low} do not depend on small variations in the effective masses or in the static dielectric constant, so that our values for B/B_{low} will be unaffected by possible future refinements of silicon parameters.

In the symmetrical plasma ($n=p$), we determine the injection dependence of B with the first experimental approach, using the well-established data of Schlangenotto *et al.*[3] While Eq. (1) predicts that j_γ is proportional to np, the measurements depicted in Fig. 1 of Ref. 3 deviate from this simple behavior, which we plot in our Fig. 1 in terms of B/B_{low} (symbols). The data scatter considerably above $B/B_{\text{low}}=0.8$, partly because our digital scan of the plot in Ref. 3 has a limited precision, and partly due to the restricted accuracy of the original experiments. At lower values of B/B_{low}, the data show that B declines with increasing injection density in a temperature-dependent manner.

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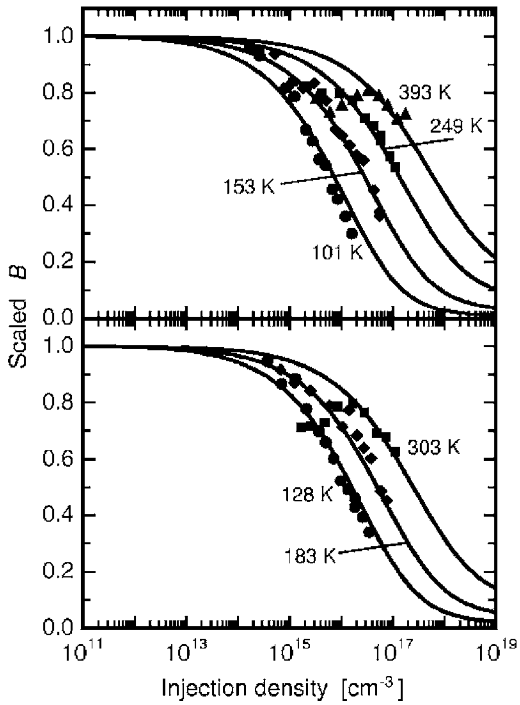

FIG. 1. The scaled radiative recombination coefficient B/B_{low} for a symmetrical plasma ($n=p$) at various temperatures. B_{low} is obtained at very low carrier densities. Symbols: measurements, as extracted from Ref. 3; lines: our calculations.

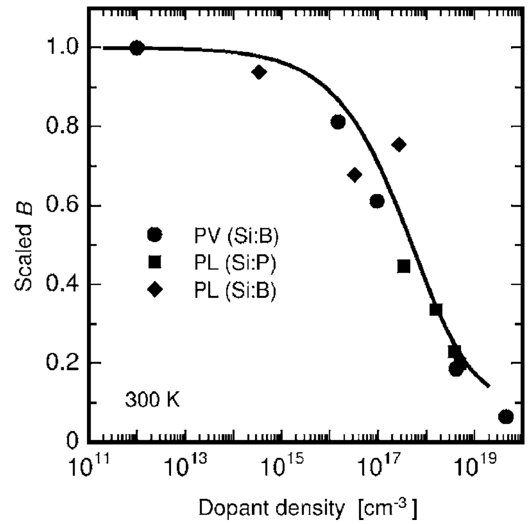

FIG. 2. The radiative recombination coefficient B for the asymmetrical plasma ($n \neq p$) at 300 K, scaled to B/B_{low}. Symbols: our measurements obtained using photovoltaic (PV) and photoluminescence (PL) methods; lines: our calculations.

In the asymmetrical case ($n \neq p$), we determine B with the second experimental approach, where α_{bb} is required for various phosphorus or boron dopant densities N_{dop}. At high N_{dop}, spectroscopic transmission measurements do not render α_{bb}, but rather the sum of α_{bb} and the coefficient for free-carrier absorption α_{fc}; the latter may completely dominate at the photon energies E_{ph} of interest. To circumvent this obstacle, we obtain α_{bb} from PL spectra in the same way as in Ref. 10, i.e., from relative measurements of the photon flux per energy interval and by applying[7]

$$\alpha_{\text{bb}} \propto \frac{dj_\gamma}{dE_{\text{ph}}} E_{\text{ph}}^{-2} e^{E_{\text{ph}}/kT}. \tag{3}$$

As it is difficult to measure dj_γ in absolute units, we scale dj_γ such that the resulting α_{bb} matches well-established data from spectroscopic transmission measurements[11] in a suitable photon energy range. In order to calculate B from these absorption data, we apply Eq. (2) involving $n_{i,\text{eff}}$ and N. We obtain $n_{i,\text{eff}}$ via

$$n_{i,\text{eff}} = n_i e^{\Delta E_g/(2kT)}, \tag{4}$$

where the intrinsic carrier density n_i is taken from Ref. 12 and the band gap shrinkage ΔE_g from Ref. 13. Finally, we use N given in Ref. 14 for lowly doped silicon because the changes in N due to doping are negligibly small.[15] The resulting B and B/B_{low} values are depicted in Fig. 2; they decline with increasing hole or electron density.

To complement these data, we fabricated solar cells with wafers of various boron dopant densities,[16] and we determined α_{bb} with spectral response measurements as in Refs. 17 and 18. As the cells are only 250 μm thin, free-carrier absorption attenuates the incoming light only at very high N_{dop}, where we correct the data with ray-tracing techniques (the optical properties of the cells are known very precisely). Because individual devices of various dopant densities are used, B/B_{low} cannot be determined directly. Instead, we calculate B from the absorption data in absolute terms via Eq. (2) and scale it to B/B_{low}, which is independent of the choice of n_i and N. Our results are plotted in Fig. 2 as circles; they coincide with the PL data shown as squares.

In the following, we outline our calculations of the injection dependence of B, shown as lines in Figs. 1 and 2. The radiative recombination is influenced by the Coulomb attraction between the electrons and holes, which increases the band-to-band recombination coefficient from its hypothetical free-carrier value B_0 to the empirical value $B=g_{eh}B_0$. The factor g_{eh} accounts for the enhanced probability of finding an electron and a hole in the immediate vicinity of each other and is given by the pair correlation function at zero interparticle distance. In contrast to Schlangenotto *et al.*,[3] who described the electron-hole interaction in terms of the bare Coulomb potential, we incorporate screening effects by employing the Debye potential. This is given by $w_{eh}(r)=-e^2/(4\pi\epsilon_r\epsilon_0)\exp(-\kappa r)/r$, where ϵ_r and ϵ_0 are the relative and vacuum dielectric constants, respectively, r is the distance and κ is the inverse screening length. A Padé approximation[19] has been used to obtain κ as a function of the carrier densities n and p. Denoting the radial s-wave functions for the relative motion of the two charge carriers by $R_{\nu 0}(r)$, there holds

$$g_{eh} = \frac{\Lambda_{eh}^3}{4\pi} \sum_\nu |R_{\nu 0}(0)|^2 \exp(-E_{\nu 0}/kT), \tag{5}$$

where $\Lambda_{eh}^2 = 2\pi\hbar^2/kTm_{eh}$ is the thermal wavelength squared and m_{eh} is the reduced electron-hole mass. The summation index ν comprises both discrete and continuous quantum numbers. The energy levels $E_{\nu 0}$ and wave functions $R_{\nu 0}(r)$ in Eq. (5) vary with κ, so that g_{eh} depends not only on the temperature T but also on the particle densities. This is a direct consequence of the screening effect. In particular, when Boltzmann statistics can be applied, one has $\kappa^2=(e^2/kT\epsilon_r\epsilon_0)(n+p)$, and the enhancement factor becomes a function of $n+p$. The bound-state portion of g_{eh} has been computed from a variational solution of the radial

Schrödinger equation by means of the quadrature discretization method;[20–22] the details of our procedure are given in Ref. 23. The scattering state portion of g_{eh} has been derived from the Noyes-Kowalski half-shell functions[24,25] for the two-particle T matrix, as outlined in Refs. 26 and 27. For low carrier densities ($\kappa \rightarrow 0$), our numerical results correctly reproduce the analytical results for the bare Coulomb potential given in Ref. 28. For high carrier densitites ($\kappa \rightarrow \infty$), g_{eh} decreases to unity because the screening is then so strong that the electron-hole system can be described by the Hartree-Fock approximation. From Eq. (5) and the Boltzmann expression for κ given above, it can be seen that the decrease of g_{eh} sets in at lower carrier densities when the temperature is reduced.

The theoretical curves describe the experiments well within the measurement's precision, as shown in Figs. 1 and 2. It has to be kept in mind that the experimental values in the asymmetrical plasma were obtained with either $n \gg p$ or $n \ll p$, while the calculations were performed for the symmetrical plasma ($n=p$). We can compare the two because at carrier densities below around 2×10^{19} cm^{-3}, Boltzmann statistics are valid, and g_{eh} is a function of $n+p$.

In order to obtain the absolute values of B, B/B_{low} needs to be multiplied with the experimentally determined B_{low} values published in Ref. 7.

In conclusion, we experimentally confirmed that the radiative recombination coefficient B in crystalline bulk silicon depends on the injection density of free carriers, and we explained our measurements in terms of numerical results for the electron-hole pair correlation function using Debye screening. We showed that B/B_{low} (with B_{low} obtained at very low carrier densities) decreases with increasing carrier densities and that this decrease starts at lower carrier densities as the temperature is reduced.

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