

Temperature dependence of the radiative recombination coefficient of intrinsic crystalline silicon

T. Trupke^{a)} and M. A. Green

Centre of Excellence for Advanced Silicon Photovoltaics and Photonics, University of New South Wales, Sydney 2052, NSW, Australia

P. Würfel

Institut für Angewandte Physik, Universität Karlsruhe, Karlsruhe, Germany

P. P. Altermatt

Australian National University, Engineering, Canberra, 0200, ACT Australia

A. Wang, J. Zhao, and R. Corkish

Centre of Excellence for Advanced Silicon Photovoltaics and Photonics, University of New South Wales, Sydney 2052, NSW, Australia

(Received 3 June 2003; accepted 25 July 2003)

The radiative recombination coefficient $B(T)$ of intrinsic crystalline silicon is determined as a function of temperature over the temperature range 77–300 K. We observe that $B(T)$ decreases as a function of temperature and we compare our results to previously published contradictory data from the literature. The radiative recombination coefficient is calculated from the absorption coefficient for band-to-band transitions, which we determine at different temperatures from photoluminescence spectra measured on planar high resistivity float zone silicon wafers. Photoluminescence spectra could be detected over a large range of more than five orders of magnitude, which allowed us to determine extremely low values of the absorption coefficient in the spectral range where absorption processes are accompanied by the simultaneous absorption of up to four phonons. © 2003 American Institute of Physics. [DOI: 10.1063/1.1610231]

I. INTRODUCTION

Crystalline silicon is the workhorse of the microelectronic industry and it also has an unrivaled role in the photovoltaic industry. Even the prospects for the development of efficient light emitting devices based on bulk crystalline silicon have improved strongly since external electroluminescence quantum efficiencies close to 1% and external photoluminescence (PL) quantum efficiencies exceeding 10% have recently been reported.^{1,2} Accurate data for the temperature variation of the absorption coefficient for band-band transitions $\alpha_{BB}(\hbar\omega, T)$ and of the radiative recombination coefficient $B(T)$ are required for the understanding of the temperature dependence of the light emitting properties of crystalline silicon and for the modeling of silicon devices.

We determine the absorption coefficient for band-band transitions $\alpha_{BB}(\hbar\omega, T)$ from PL spectra. The integral radiative recombination coefficient $B(T)$ is calculated from these data using the van Roosbroeck theory. Some contradictory experimental results from the literature for the temperature dependence of $B(T)$ of silicon are discussed.

II. THEORY

A. Radiative recombination coefficient $B(T)$

For nondegenerate occupation of the bands the spontaneous radiative recombination rate per energy interval $dr_{sp}(\hbar\omega)$ of electrons and holes via band-band transitions inside a semiconductor can be described by

$$dr_{sp}(\hbar\omega, T) = B(\hbar\omega, T) \cdot n_e \cdot n_h \cdot d(\hbar\omega) \quad (1)$$

with n_e and n_h the electron and hole concentrations, respectively, and $B(\hbar\omega, T)$ the spectral radiative recombination coefficient as a function of the photon energy $\hbar\omega$ and of temperature T . The rate of spontaneous emission in an excited semiconductor is also described by the generalized Planck equation:³

$$dr_{sp}(\hbar\omega, T) = \frac{(\hbar\omega)^2 \cdot n^2}{\pi^2 \hbar^3 c_0^2} \cdot \alpha_{BB}(\hbar\omega, T) \cdot \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\eta}{kT}\right) - 1} d(\hbar\omega) \quad (2)$$

which is an extended form of the van Roosbroeck equation, which, in its original form is valid only for thermal emission.⁴ Equation (2) can be simplified for nondegenerate occupancies of the bands to

$$dr_{sp}(\hbar\omega, T) = \frac{(\hbar\omega)^2 \cdot n^2}{\pi^2 \hbar^3 c_0^2} \cdot \alpha_{BB}(\hbar\omega, T) \cdot \exp\left(\frac{\Delta\eta - \hbar\omega}{kT}\right) \cdot d(\hbar\omega). \quad (3)$$

In Eqs. (2) and (3), n denotes the energy- and temperature-dependent refractive index and $\Delta\eta$ the separation of the quasi-Fermi energies. In a general case a similar expression to that for the band-band transitions, but with $\Delta\eta=0$, should be included for free carrier emission in Eqs. (2) and

^{a)}Electronic mail: thorsten@trupke.de

(3). However, under even moderate excitation conditions as in typical photoluminescence measurements the band–band transitions dominate the emission totally and the reverse of parasitic absorption processes, such as free carrier absorption, can be neglected.⁵ Inserting the relation

$$n_e \cdot n_h = n_i^2 \cdot \exp\left(\frac{\Delta \eta}{kT}\right)$$

into Eq. (1), with n_i the intrinsic carrier concentration, $B(\hbar\omega, T)$ can be determined from Eqs. (1) and (3) as

$$B(\hbar\omega, T) = \frac{1}{n_i^2} \frac{(\hbar\omega)^2 \cdot n^2}{\pi^2 \hbar^3 c_0^2} \cdot \alpha_{BB}(\hbar\omega, T) \cdot \exp\left(\frac{-\hbar\omega}{kT}\right). \quad (4)$$

The total radiative recombination rate $R(T)$ is obtained by integrating Eq. (1) over the entire spectrum, yielding $R(T) = B(T) \cdot n_e \cdot n_h$, with the integral radiative recombination coefficient $B(T)$ given by

$$B(T) = \frac{1}{n_i^2} \frac{1}{\pi^2 \hbar^3 c_0^2} \cdot \int_0^\infty n^2 \cdot (\hbar\omega)^2 \cdot \alpha_{BB}(\hbar\omega, T) \cdot \exp\left(\frac{-\hbar\omega}{kT}\right) \cdot d(\hbar\omega). \quad (5)$$

$$A(\hbar\omega) = \frac{[1 - R_f(\hbar\omega)] \cdot (1 - e^{-\alpha_{BB}(\hbar\omega)d}) \cdot [1 + R_b(\hbar\omega)e^{-\alpha_{BB}(\hbar\omega)d}]}{1 - R_f(\hbar\omega)R_b(\hbar\omega)e^{-2\alpha_{BB}(\hbar\omega)d}} \quad (7)$$

with $R_f(\hbar\omega)$ and $R_b(\hbar\omega)$ the reflectance of the front and of the rear surface, respectively, and d the thickness of the sample.

The expression for the absorptance [Eq. (7)] simplifies to $A(\hbar\omega) = \alpha_{BB}(\hbar\omega)d$ if the reflectance of the front surface and of the rear surface are identical and under the assumptions of negligible reabsorption of internally generated photons by band–band transitions, which is described by $\alpha_{BB}(\hbar\omega)d \ll 1$. Eq. (6) then simplifies to

$$dj_{\gamma,em} = \frac{\alpha_{BB}(\hbar\omega) \cdot d}{4\pi^2 \hbar^3 c_0^2} \cdot (\hbar\omega)^2 \exp\left(\frac{-\hbar\omega}{kT}\right) \cdot \exp\left(\frac{\Delta \eta}{kT}\right) d(\hbar\omega). \quad (8)$$

In this case division of the experimentally determined emitted photon flux per energy interval by

$$(\hbar\omega)^2 \cdot \exp\left(\frac{-\hbar\omega}{kT}\right)$$

yields the absorption coefficient in relative units.

B. Determination of $\alpha_{BB}(\hbar\omega)$ from PL

Accurate data for the absorption coefficient for band–band transitions are required for the calculation of $B(T)$ according to Eq. (5). The determination of the absorptance and of the absorption coefficient from luminescence spectra has been described in detail in Refs. 5 and 6. The photon flux per energy interval $dj_{\gamma,em}$ emitted by a sample into a hemisphere is described by a generalized form of Kirchhoff's law⁵

$$dj_{\gamma,em} = \frac{(\hbar\omega)^2}{4\pi^2 \hbar^3 c_0^2} \cdot A(\hbar\omega) \cdot \exp\left(\frac{-\hbar\omega}{kT}\right) \cdot \exp\left(\frac{\Delta \eta}{kT}\right) d(\hbar\omega), \quad (6)$$

with $A(\hbar\omega)$ the absorptance of the sample. This simplified form of the generalized Kirchhoff's law is valid only for nondegenerate occupancies of the bands and if reabsorption of internally generated photons on their way through the sample by free carrier absorption is negligible, which are reasonable assumptions in our study of high resistivity silicon wafers under mild accumulation conditions. In that case the absorptance of a planar sample in Eq. (6) is the absorptance for band–band transitions⁵ and can be written as

III. METHODS

A. Prior studies of $B(T)$ and choice of method

Equations (1) and (5) suggest two different experimental approaches for the determination of $B(T)$.

(1) From Eq. (5) $B(T)$ can be calculated if the spectral dependence of the absorption coefficient for band–band transitions and the intrinsic carrier concentration are known at a range of temperatures. Michaelis and Pilkuhn⁷ calculated $B(T)$ for silicon using experimental data for the absorption coefficient published by MacFarlane *et al.*⁸ Varshni calculated $B(T)$ from Eq. (5) using theoretical values for the absorption coefficient.⁹ Figure 1 shows the data calculated by Michaelis and Pilkuhn (open squares) and by Varshni (open circles), respectively. Both predict an increasing value of $B(T)$ with increasing temperature and a value of roughly 1.7×10^{-15} cm³/s at room temperature. Using theoretical data for the absorption coefficient of silicon, Ruff *et al.* determined a radiative recombination coefficient of approximately 7×10^{-15} cm³/s (diamond in Fig. 1) at room temperature.¹⁰

The elegance of this procedure of determining $B(T)$ lies in the fact that absolute measurements of the emitted photon flux, which are always associated with comparatively large experimental errors, are avoided.

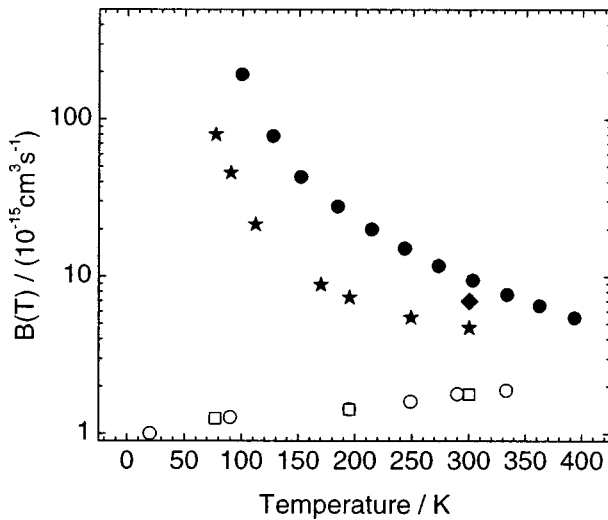


FIG. 1. Comparison of our data for the radiative recombination coefficient $B(T)$ with data from the literature. Stars: this study, Full circles: Schlangenotto *et al.* (Ref. 11); Open circles: Varshni (Ref. 9); Open squares: Michaelis *et al.* (Ref. 7); Diamond: Ruff *et al.* (Ref. 10).

(2) $B(T)$ can be determined from Eq. (1) by measuring the rate of spontaneous emission and the carrier concentrations n_e and n_h , respectively. Following that approach Schlangenotto *et al.* determined the rate of spontaneous emission from quantitative electroluminescence measurements on silicon pin devices.¹¹ The carrier concentrations of electrons and holes inside the device were determined by integrating the time dependent current after short-circuiting the diode. Reabsorption of spontaneously emitted photons was qualitatively taken into account in these calculations. In contrast to the data presented in Refs. 7 and 9 Schlangenotto *et al.* find that the radiative recombination coefficient decreases strongly with increasing temperature (full circles in Fig. 1). At $T=300$ K they determine a value of $B=0.95 \times 10^{-14} \text{ cm}^3/\text{s}$.

Figure 1 clearly shows that the literature data for the radiative recombination coefficient vary substantially throughout the temperature range 70–300 K by up to two orders of magnitude at low temperatures.

Here we are using the same approach as in Refs. 7 and 9, i.e., we calculate $B(T)$ from the absorption coefficient for band–band transitions. One problem that arises using this method is that, especially at low temperatures, photons are spontaneously emitted in a spectral range in which the absorption coefficient $\alpha_{\text{BB}}(\hbar\omega, T)$ takes on values which are too small to be determined accurately with transmission experiments. For example, very accurate data for the absorption coefficient have been determined by MacFarlane *et al.*⁸ We scanned and digitized their published graphical results and calculated the rate of spontaneous emission according to Eq. (3). As an example, the rate of spontaneous emission calculated from MacFarlane's data are shown in Fig. 2 for $T=363$ K, $T=249$ K, and for $T=112$ K. Figure 2 clearly demonstrates that the data by MacFarlane are unsuitable for the calculation of $B(T)$ at temperatures above room temperature and also at lower temperatures because at these temperatures more data would be required for an accurate integration

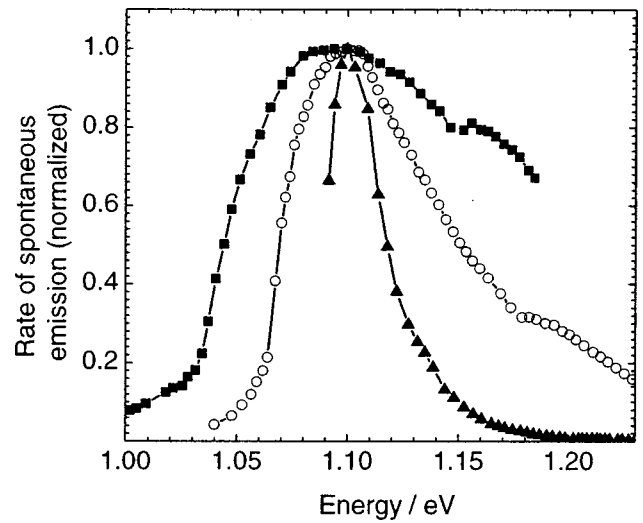


FIG. 2. Rate of spontaneous emission calculated according to Eq. (3) using data for the absorption coefficient from Ref. 8 at $T=363$ K (squares), $T=249$ K (open circles), and $T=112$ K (triangles).

over the entire spectrum at the high- and the low-energy side of the spectrum, respectively.

Two methods have been demonstrated by which extremely small values of the absorption coefficient $\alpha_{\text{BB}}(\hbar\omega, T)$ can be determined. Keevers and Green used spectral response measurements on textured silicon solar cells to determine $\alpha_{\text{BB}}(\hbar\omega, T)$ at room temperature.¹² Daub and Würfel determined $\alpha_{\text{BB}}(\hbar\omega, T)$ from PL spectra.⁶ With these methods values of the absorption coefficient as low as $\alpha_{\text{BB}}(\hbar\omega, T)=3 \times 10^{-8} \text{ cm}^{-1}$ could consistently be determined at room temperature, values that could never be determined with a conventional transmission experiment. An additional problem with transmission experiments arises at photon energies below the band-gap energy due to the fact that free carrier absorption completely masks the small absorption coefficient for band–band transitions.

Here, we determined the absorption coefficient $\alpha_{\text{BB}}(\hbar\omega, T)$ at different temperatures from PL spectra measured on high resistivity silicon wafers.

B. Intrinsic carrier concentration n_i

The intrinsic carrier concentration n_i is required at each temperature for the calculation of $B(T)$. The accuracy of these data critically affects the accuracy of $B(T)$ because the square of n_i enters Eq. (5). Data for n_i of silicon as a function of temperature have been published by Sproul and Green¹³ and independently by Misiakos and Tsamakis.¹⁴ The temperature dependence of their data can be described by the analytical expression:

$$n_i(T) = 2.9135 \times 10^{15} \cdot T^{1.6} \cdot \exp\left(-\frac{E_g(T)}{2kT}\right), \quad (9)$$

with $E_g(T)$ the temperature dependent band-gap energy of silicon according to Ref. 15. The inset of Fig. 3 highlights the relative deviation of Sproul's and of Misiakos' data from

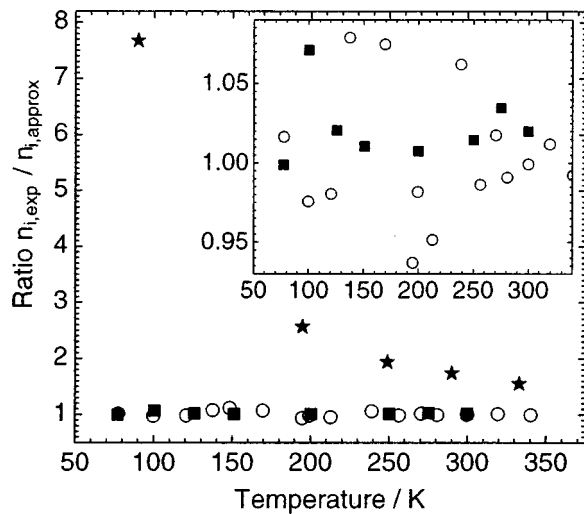


FIG. 3. Relative deviations of published data for the intrinsic carrier concentration n_i from the approximate formula in Eq. (9). Stars: Varshni (Ref. 9), full squares: Sproul and Green (Ref. 13), open circles: Misiakos and Tsamakis (Ref. 14). The inset demonstrates that Misiakos' and Sproul's data deviate less than 8% relatively from Eq. (9) (except for one data point in Misiakos' data).

the analytic expression in Eq. (9). Except for one data point in Misiakos' data all data deviate less than 8% from the analytic expression.

Equation (9) predicts a value $n_i = 9.71 \times 10^9 \text{ cm}^{-3}$, at $T = 300 \text{ K}$ which is, in terms of measurement precision, significantly below the value determined by Sproul and Green but which is in excellent agreement with Misiakos' data. Recently, Green and Sproul's data were reinterpreted,¹⁶ taking into account the effect of band-gap narrowing at low dopant densities.¹⁷ The resulting n_i is $n_i = 9.65 \times 10^9 \text{ cm}^{-3}$ at $T = 300 \text{ K}$, which deviates from the value calculated according to Eq. (9) by less than 1%.

In our experiment, the carrier injection density reaches up to 10^{16} cm^{-3} , which causes a considerable amount of free-carrier induced band-gap narrowing¹⁷ and, in turn, increases the intensity of the PL signal. Hence, the question arises¹⁶ as to whether n_i is appropriate to use in Eq. (4), or whether n_i should be replaced by the effective intrinsic density $n_{i,\text{eff}}$:

$$n_{i,\text{eff}} = n_i \cdot \exp\left(\frac{\Delta E_G}{2kT}\right). \quad (10)$$

In our experiment, it is not necessary to determine the absolute PL intensity, as we transform our measured PL spectrum to α_{BB} and pin the latter to data received by transmission spectroscopy. It is the injection density present when the latter data were received that determines the choice between n_i and $n_{i,\text{eff}}$. During transmission measurements, the injection density is very low, justifying our use of n_i .

C. Refractive index $n(\hbar\omega, T)$

The energy and temperature dependence of the refractive index n is required for the calculation of $B(T)$. At room temperature we used literature data for the refractive index from Ref. 18. At lower temperatures we calculated the tem-

perature and energy dependence of the refractive index in the spectral range where luminescence occurs, i.e., around $\hbar\omega = 1.1 \text{ eV}$, using an approximate formula for the refractive index derived by Ellison and Modine.¹⁹ These authors determined the refractive index only at photon energies $\hbar\omega > 1.45 \text{ eV}$ and at temperatures above room temperature. The approximate formula [Eq. (7) in Ref. 19] thus actually represents an extrapolation into a temperature range and into a photon energy range not covered by the experimental data in Ref. 19. However, in the spectral range around 1.1 eV and for room temperature we observe deviations between the approximate formula and the data in Ref. 18 of less than 1%. Measurements of the refractive index at low temperatures have been published by Icenogle *et al.* for different wavelength below the direct band-gap energy of silicon.²⁰ Again we find only marginal deviations of less than 1% between the experimental data for $\lambda = 2.554 \mu\text{m}$ (the shortest wavelength investigated in Ref. 20) and the approximate formula.

We conclude that due to the relatively weak dependence of the refractive index on temperature and on the photon energy in the spectral range around 1.1 eV the use of the approximate formula from Ref. 19 introduces a small relative error of less than 2% for the calculated values of $B(T)$.

D. Experiment

PL spectra were measured using laser radiation from a 50 mW, 785 nm laser diode that was passed through a 785 nm interference filter to excite the sample. The PL signal was passed through an Oriel Ms260i 1/4 m monochromator with a grating blazed at 1200 nm. A liquid nitrogen cooled In-GaAs diode with an active area of 1 mm^2 and with a built-in preamplifier with a transimpedance of 10^9 V/A was used as detector. The signal was measured by standard lock-in technique with a modulation frequency of the incident laser of 12 Hz. The sample was mounted on the cold finger of a closed cycle liquid helium cryostat. The temperature was measured with a silicon diode mounted on the cold finger. We checked that the laser did not significantly heat the sample by comparison of spectra measured at a given temperature with variable laser power. The relative spectral sensitivity of the whole setup was calibrated against a calibrated 200 W-QTH-lamp purchased from Oriel.

A double-side polished $300 \mu\text{m}$ thick, $1000 \Omega \text{ cm}$ n -type silicon wafer was investigated. Both surfaces of the wafer were passivated by oxides thermally grown in TCA (1,1,1 trichloroethane) ambient. Furthermore, the surfaces were aluminum annealed (Alannealed)²¹ to improve the surface passivation. In our PL experiments the surfaces were charged using a static discharge. Charging of the oxides on both sides of the wafer further reduces the surface-recombination velocity and results in a significant increase of the PL signal. The oxide thickness on each side of the wafer was 178 nm as determined with an ellipsometer. This thickness of the oxide was chosen as it corresponds to a minimum in the reflectance in the spectral range, where luminescence is emitted. The spectral reflectance, which is required according to Eq. (7) for the numerical calculation of the absorption coefficient from the absorptance at higher energies, was measured with

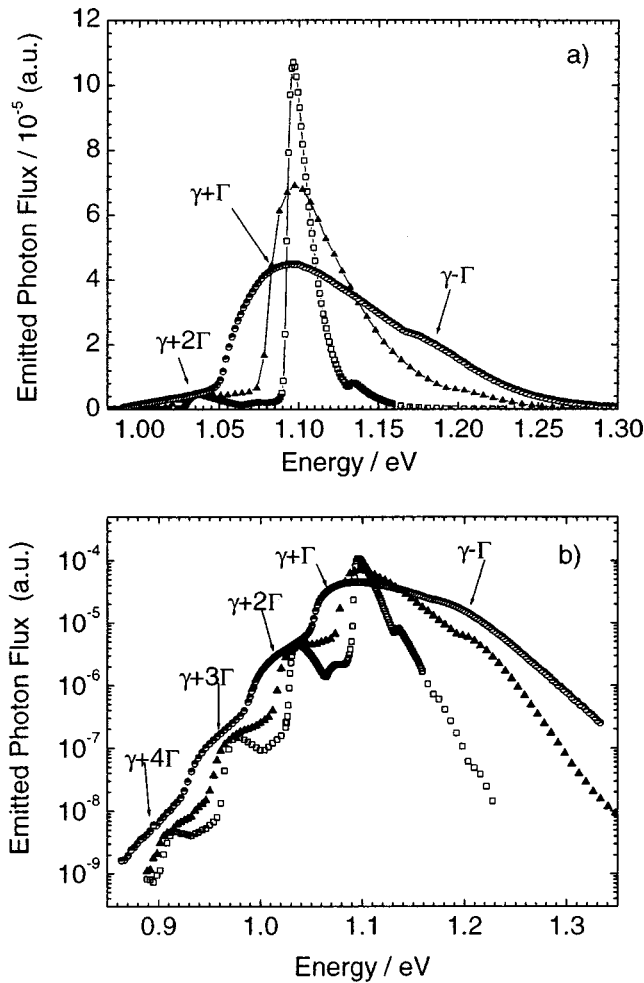


FIG. 4. PL spectra of a planar 300 μm thick silicon sample measured at $T=291$ K (circles), $T=170$ K (triangles) and $T=77$ K (squares); (a) linear scale; (b) semilogarithmic scale.

a Cary spectrophotometer and was found to be identical for each side of the wafer.

E. Absorption coefficient $\alpha_{\text{BB}}(\hbar\omega)$

The sensitivity of our experimental setup and the high quality of the samples allowed measurements of the PL spectrum over more than five orders of magnitude into the spectral range where the emission of a photon is accompanied by the simultaneous emission of four phonons. As an example, Fig. 4 shows PL spectra measured at $T=291$ K, $T=170$ K, and $T=77$ K on (a) linear and on (b) semilogarithmic scales. The signal is completely dominated by phonon-assisted recombination of electron hole pairs, i.e., by indirect band-to-band transitions. Above and below the band-gap energy, photon emission is accompanied by phonon absorption and phonon emission, respectively. In Fig. 4 the humps in the spectrum that correspond to the emission of photons with absorption and emission of variable numbers of phonons are indicated. For example $\gamma+\Gamma$ indicates that a photon and one phonon are simultaneously emitted or absorbed in an optical transition, while $\gamma-\Gamma$ indicates the spectral range in which photon emission is accompanied by phonon absorption and photon absorption is accompanied by phonon emission.

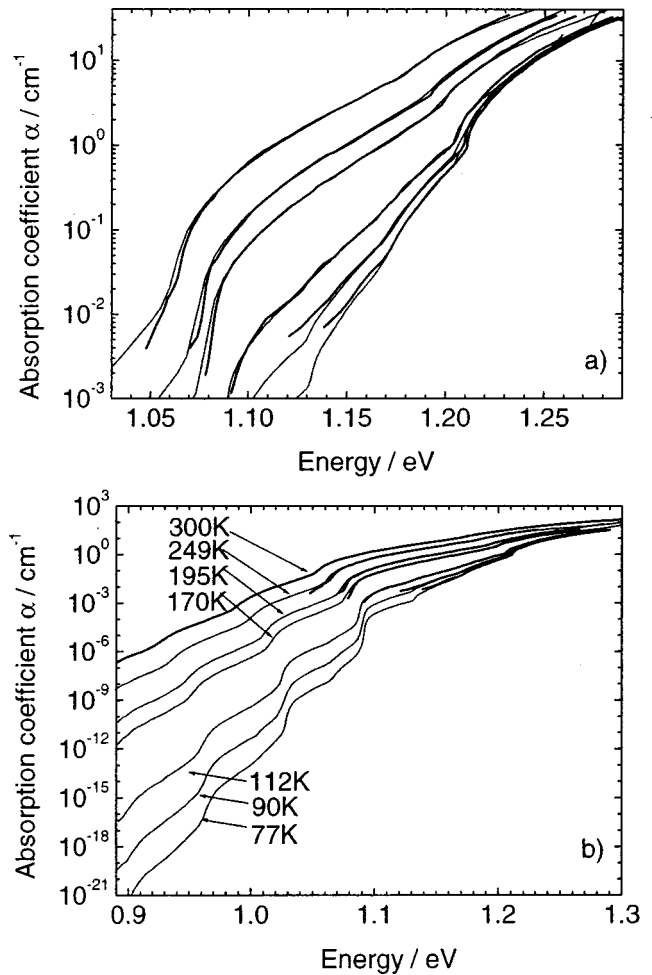


FIG. 5. Absorption coefficient for band-to-band transitions of silicon at temperatures 249, 195, 170, 112, 90, and 77 K. The data were determined from the PL spectra, some of which are shown in Fig. 4. The values from PL were scaled to the data published by MacFarlane *et al.* (Ref. 8) (the latter shown as thick lines): (a) highlights the overlap spectral region covered by MacFarlane's data. The data by Green and Keevers (Ref. 18), which we used for the calculations at $T=300$ K are included in (b) (upper curve) for comparison.

Relative values of the absorbance $A(\hbar\omega)$ were calculated according to Eq. (6) from these spectra by dividing the emitted photon flux per energy interval by

$$(\hbar\omega)^2 \cdot \exp\left(-\frac{\hbar\omega}{kT}\right).$$

In the low energy range of the spectrum, where $\alpha_{\text{BB}}(\hbar\omega)d \ll 1$, these relative values for $A(\hbar\omega)$ are representative of the relative variation of $\alpha(\hbar\omega)$, which could be scaled to MacFarlane's data. Multiplication of the scaled data by the thickness d then yields absolute values for the absorbance from which the absorption coefficient is subsequently determined numerically throughout the entire spectrum. The absorption coefficient data obtained from PL spectra at different temperatures with this method are shown together with MacFarlane's data in Fig. 5(a) are shown together with MacFarlane's data in Fig. 5. Very good agreement is observed at all temperatures over a wide spectral range in the overlap region

where literature data are available and where the absorption coefficient can be determined accurately from the PL spectra

At the low energy end of MacFarlane's data we observe deviations from our data. These deviations occur in a spectral range where the absorption coefficient takes on values on the order of 10^{-2} cm^{-1} , which are difficult to determine with transmission and reflection experiments. We therefore believe that our data are more accurate in this regime. In addition a particularly large relative error is introduced for the lowest values of the absorption coefficient by the digitization of MacFarlane's data.

Deviations between our data and MacFarlane's data are also observed at large energies. The absorbance of our samples saturates at these energies and small experimental errors for the absorbance result in very large relative errors for the absorption coefficient determined with our method. MacFarlane's data are more accurate in that spectral range because thinner silicon samples were investigated for the determination of the absorption coefficient at large photon energies. In addition, the determination of the absorbance from PL spectra according to Eq. (6) is based on the assumption of a homogeneous carrier concentration. Residual surface recombination, which is present at a low level despite the excellent surface passivation in our samples, leads to an inhomogeneous carrier concentration, in particular near the surfaces. Such nonhomogeneities affect the relative distribution of the emitted photons and make the analysis of PL spectra impossible at high energies without knowledge of the exact spatial distribution of the carrier concentration. For this reason we used literature data for the absorption coefficient at $T=300 \text{ K}$ taken from Ref. 18 to calculate $B(T)$ at room temperature. At lower temperatures the emission is determined by much lower values of the absorption coefficient, which can be determined accurately from PL spectra despite inhomogeneities in the carrier distribution.⁶

IV. RESULTS

A. Radiative recombination coefficient $B(T)$

The integration of the absorption coefficient according to Eq. (5) at different temperatures using the data sets shown in Fig. 5 and using the intrinsic carrier concentration according to Eq. (9) yields the temperature dependence of $B(T)$. The refractive index was calculated according to Eq. (7) in Ref. 19, except for $T=300 \text{ K}$, where the data from Ref. 18 were used. The integrated rate of spontaneous emission, the intrinsic carrier concentration and the radiative recombination coefficient $B(T)$ are listed in Table I. The data for $B(T)$ are also shown in Fig. 1 (stars) in comparison to Michaelis' data (open squares), Varshni's data (open circles), Schlengenotto's data (full circles) and Ruff's data (diamond).

V. DISCUSSION

A. Comparison with Schlengenotto's data

In agreement with Schlengenotto's data, we find a strongly decreasing radiative recombination coefficient $B(T)$ with increasing temperature. This relative variation of $B(T)$ is also in qualitative agreement with the observation in Ref. 2

TABLE I. Integral rate of spontaneous emission, intrinsic carrier concentration according to Eq. (9) and radiative recombination coefficient $B(T)$ according to Eq. (5) at different temperatures. The data for the absorption coefficient and for the refractive index at $T=300 \text{ K}$ were taken from Ref. 18 in preference to the calculation of the absorption coefficient from PL.

Temperature (K)	$\int_0^\infty dr_{sp}(\hbar\omega)d(\hbar\omega)$ ($\text{s}^{-1} \text{ cm}^{-3}$)	n_i (cm^{-3})	$B(T)$ ($\text{cm}^3 \text{ s}^{-1}$)
77	3.04×10^{-53}	1.95×10^{-20}	8.01×10^{-14}
90	3.59×10^{-42}	8.87×10^{-15}	4.57×10^{-14}
112	2.92×10^{-29}	3.69×10^{-8}	2.14×10^{-14}
170	6.27×10^{-11}	84.21	8.84×10^{-15}
195	2.66×10^{-6}	19000	7.35×10^{-15}
249	21.08	6.20×10^7	5.48×10^{-15}
300	445784	9.71×10^9	4.73×10^{-15}

that starting at room temperature the integral luminescence intensity increases with decreasing temperature despite decreasing effective excess carrier lifetimes, i.e., despite decreasing carrier concentrations. According to Eq. (1), this observation can be explained only by an increasing radiative recombination coefficient with decreasing temperature.

Our data are, however, a factor two to four smaller than Schlengenotto's data.¹¹ These deviations are most likely due to inaccuracies associated with the experimental technique used in Ref. 11, which involves the quantitative determination of the rate of spontaneous emission from the measured emitted photon flux. First, the integral photon flux emitted into a hemisphere was determined quantitatively, which introduces an estimated relative experimental error of 20%–30%. Second, the reabsorption of internally generated photons on the way to the surface must be taken into account. In Ref. 11 this was done only qualitatively using an effective absorption coefficient. A more accurate method to determine the ratio between the emitted photon flux and the rate of spontaneous emission has recently been presented in Ref. 22. Comparison of the qualitative estimation of the effect of reabsorption used in Ref. 11 with the correct theory we estimate another relative error of 20% at room temperature in Schlengenotto's data.

Most importantly, however, roughness of device surfaces can lead to an increase of the emitted photon flux by up to a factor $2n^2$ (~ 25 for silicon) compared to the photon flux emitted by a device with planar surfaces with the same internal rate of spontaneous emission. This effect has been demonstrated, e.g., in Ref. 1, where texturing of the surface resulted in a tenfold increase of the emitted photon flux. According to another publication by Schlengenotto's group,²³ the edge of their device, through which the emission was monitored, was polished. However, even if the emitting surface itself is planar, any roughness of other surfaces of the device also strongly affects the fraction of internally generated photons that eventually escape and contribute to the emitted photon current. We believe that this effect can easily lead to an overestimation of the rate of spontaneous emission by a factor of three, which, together with the other sources of experimental error discussed above, could explain the deviations from our data.

B. Comparison with Michaelis and Varshni data

Two major sources of error can be identified for the data published in Refs. 7 and 9. The most important error stems from inaccurate values for the intrinsic carrier concentration n_i . The relative deviation of the data for n_i used in Refs. 7 and 9 from the formula in Eq. (9) is shown in Fig. 3. Varshni's data exceed the data calculated from the analytic expression by roughly 55% at room temperature and by more than a factor 7 at lower temperatures. Especially at low temperatures this overestimation of n_i leads to a dramatic underestimation of $B(T)$ by more than a factor 50! The smaller overestimation of n_i results in a much smaller underestimation of $B(T)$ by less than a factor three at higher temperatures, leading to the erroneous determination of an increasing dependence of $B(T)$ as a function of temperature. The fact that Michaelis and Varshni both used identical data for n_i also explains the excellent agreement between their calculated data for $B(T)$. Inaccurate data for n_i were already identified by Wasserrab²⁴ as the major source of error in Varshni's calculations of $B(T)$. However, Wasserrab claimed in a subsequent article²⁵ that the effects of Coulomb interaction and of excitonic recombination needed to be accounted for in the calculations of $B(T)$. While the $B(T)$ values initially published in Ref. 24 are in good quantitative agreement with the data presented here, the data in Ref. 25, which are based on calculations in which Coulomb enhancement and excitonic effects were explicitly taken into account, were in quantitative agreement with Schlagenotto's experimental data, which, as discussed above, are roughly a factor three too large. In his later article Wasserrab, in an attempt to match Schlagenotto's experimental data, overlooked the fact that, according to the principle of detailed balance, the effects of Coulomb enhancement and of excitonic recombination are implicitly accounted for correctly in the calculation of the intrinsic value of $B(T)$ by using experimental data for the intrinsic absorption coefficient.

A further error in the $B(T)$ values determined in Refs. 7 and 9 arises from inaccurate data for the absorption coefficient. As shown in Fig. 2 MacFarlane's data alone are not suitable to calculate the rate of spontaneous emission at temperatures below 150 K. On the other hand, the theoretical model for the absorption coefficient used by Varshni is too simplistic to describe accurately, e.g., multiphonon transitions or transitions that involve other phonons than the TO phonon.

C. Carrier density dependence of $B(T)$

It is well known that, in the band structure of Si, the valence- and conduction-band extrema do not occur at the same point in the reduced Brillouin zone, and that phonon-assisted transitions dominate the radiative recombination rate. If B were solely determined by noninteracting carriers, B would increase with increasing T because the phonon states are increasingly occupied, as expressed analytically by²⁶

$$B(T) = \frac{4\pi\epsilon\hbar^3 E_G^2 A}{c^2 (m_e m_h)^{3/2}} \frac{e^{\Theta/T} + 1}{e^{\Theta/T} - 1}, \quad (11)$$

where Θ is the effective phonon energy, m are the density-of-states masses, and A represents the amount of electron-phonon coupling. This temperature behavior of B is not observed. The reason for this is the long-range Coulomb interaction between the electrons and holes, as pointed out by Ref. 11. The electrons and holes attract each other, which causes the electron density to increase in the vicinity of a hole. This is expressed by the pair wave function $\psi_{eh}(r)$ where the considered electron and hole have distance r . As both electron and hole must be at the same space coordinate to recombine, B is enhanced by the two-particle correlation factor

$$g_{eh} = \frac{\langle |\psi_{eh}(0)|^2 \rangle}{n_e n_h}. \quad (12)$$

From Eqs. (2) and (5), we expect that Coulomb enhancement is also contained in α_{BB} . In fact, Elliott²⁷ showed that α_{BB} differs from the free-particle approximation by $|\psi(0)|^2$ as well. Calculations indicate that g_{eh} increases with decreasing temperature to the extent that it explains our measurements.²⁸ We mention that Eq. (12) does not distinguish between bound electron-hole states (excitons) and free (scattering) states, since both types of states contribute to g_{eh} . Hence, B is not only enhanced by excitons, but by Coulomb interaction in general, and the term "Coulomb enhanced B " is more appropriate than "exciton enhanced B ."

The Coulomb enhancement implies that B is not only a function of temperature, but also of the carrier densities n_e and n_h , respectively. Calculations²⁹ indicate that g_{eh} is rather constant up to injection densities of 10^{14} cm^{-3} at 70 K and 10^{16} cm^{-3} at room temperature, but drops at higher injection densities. As we do not measure the absolute PL intensity, but transform our measured PL spectrum to α_{BB} and pin it to data received by transmission spectroscopy, we are not affected by variations in g_{eh} as long as the shape of the PL spectrum is independent of the injection density. For a given T , we observe no variations in the spectral distribution when we decrease the laser intensity. This is expected because, for example, the exciton binding energy is rather constant at low injection densities.³⁰ On these grounds, our assumption of $B(T)$ instead of $B(T, n_e, n_h)$ is well justified.

VI. SUMMARY AND CONCLUSIONS

We have presented accurate data for the absorption coefficient for band-band transitions of silicon, which we determined from PL spectra of planar silicon wafers at different temperatures. The integral radiative recombination coefficient $B(T)$ of silicon was calculated from these data. We observe that $B(T)$ decreases strongly with increasing temperature and we discussed deviations between our and previously published data.

We believe that the procedure of calculating $B(T)$ from Eq. (5) using experimental data of the absorption coefficient for band-band transitions gives the most reliable results due to the inaccuracies that are always involved in the direct experimental determination of absolute values for the internal rate of spontaneous emission and of the carrier concentrations. Also, we think that it is preferable to use reliable

experimental data for the absorption coefficient rather than theoretical data as in Refs. 9 and 10, because theoretical models will always be developed on the basis of experimental data. Our study has the advantage over previous studies in which experimental data for the absorption coefficient were used, that we were able to determine extremely low values of the absorption coefficient from PL measurements. These low values of the absorption coefficient are required for the calculation of $B(T)$ especially at lower temperatures and were not available in previous studies as they are not accessible with conventional absorption measurements like transmission and reflectance experiments.

ACKNOWLEDGMENTS

The Centre of Excellence for Advanced Silicon Photovoltaics and Photonics is supported under the Australian Research Council's Centres of Excellence Scheme. One author (T.T.) would like to thank the Alexander von Humboldt foundation for a Feodor Lynen-Scholarship while another (M.A.G.) acknowledges the award of an Australian Government Federation Fellowship.

- ¹M. A. Green, J. Zhao, A. Wang, P. Reece, and M. Gal, *Nature (London)* **412**, 805 (2001).
- ²T. Trupke, J. Zhao, A. Wang, R. Corkish, and M. A. Green, *Appl. Phys. Lett.* **82**, 2996 (2003).
- ³P. Würfel, *J. Phys. C* **15**, 3967 (1982).
- ⁴W. van Roosbroeck and W. Shockley, *Phys. Rev.* **94**, 1558 (1954).
- ⁵T. Trupke, E. Daub, and P. Würfel, *Sol. Energy Mater. Sol. Cells* **53**, 103 (1998).
- ⁶E. Daub and P. Würfel, *Phys. Rev. Lett.* **74**, 1020 (1995).
- ⁷W. Michaelis and M. H. Pilkuhn, *Phys. Status Solidi* **36**, 311 (1969).
- ⁸G. G. MacFarlane, T. P. MacLean, J. E. Quarrington, and V. Roberts, *Phys. Rev.* **111**, 1245 (1958).
- ⁹Y. P. Varshni, *Phys. Status Solidi* **19**, 459 (1967).
- ¹⁰M. Ruff, M. Fick, R. Lindner, U. Rössler, and R. Helbig, *J. Appl. Phys.* **74**, 267 (1993).
- ¹¹H. Schlagenotto, H. Maeder, and W. Gerlach, *Phys. Status Solidi A* **21**, 357 (1974).
- ¹²M. J. Keevers and M. A. Green, *Appl. Phys. Lett.* **66**, 174 (1995).
- ¹³A. B. Sproul and M. A. Green, *J. Appl. Phys.* **73**, 1214 (1993).
- ¹⁴K. Misiakos and D. Tsamakis, *J. Appl. Phys.* **74**, 3293 (1993).
- ¹⁵W. Bludau, A. Onton, and W. Heinke, *J. Appl. Phys.* **45**, 1846 (1974).
- ¹⁶P. Altermatt, A. Schenk, F. Geelhaar, and G. Heiser, *J. Appl. Phys.* **93**, 1598 (2003).
- ¹⁷A. Schenk, *J. Appl. Phys.* **84**, 3684 (1998).
- ¹⁸M. A. Green and M. J. Keevers, *Prog. Photovoltaics* **3**, 189 (1995).
- ¹⁹G. E. Jellison, Jr. and F. A. Modine, *J. Appl. Phys.* **76**, 3758 (1994).
- ²⁰H. W. Icenogle, B. C. Platt, and W. L. Wolfe, *Appl. Opt.* **15**, 2348 (1976).
- ²¹J. Zhao, A. Wang, P. Altermatt, and M. A. Green, *Appl. Phys. Lett.* **66**, 3636 (1995).
- ²²T. Trupke, J. Zhao, A. Wang, and M. A. Green, paper presented at the IEEE-COMMAD conference, December 2002 in Sydney, Australia (in press).
- ²³W. Gerlach, H. Schlagenotto, and H. Maeder, *Phys. Status Solidi A* **13**, 277 (1972).
- ²⁴T. Wasserrab, *Z. Naturforsch. A* **33**, 1097 (1978).
- ²⁵T. Wasserrab, *Z. Naturforsch. A* **34**, 656 (1979).
- ²⁶W. P. Dumke, *Phys. Rev.* **105**, 139 (1957).
- ²⁷R. J. Elliot, *Phys. Rev.* **108**, 1384 (1957).
- ²⁸A. Hangleiter, Habilitation Thesis, University of Stuttgart, Germany, 2002.
- ²⁹F. Geelhaar, Technical Report No. 2/2002, ETH Zurich, Switzerland, 2002.
- ³⁰G. Manzke, Q. Y. Peng, K. Henneberger, U. Neukirch, K. Hauke, J. Gutowski, and D. Hommel, *Phys. Rev. Lett.* **80**, 4943 (1998).