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## Temperature Dependence of the Radiative Recombination Coefficient in Silicon<sup>1)</sup>

By

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The temperature dependence of the intrinsic radiative recombination coefficient  $B$  in silicon was measured from 100 to 400 °K. In contrast to previous calculations,  $B$  decreases with temperature. For interpretation of the measurements, a unique theory of the indirect radiative band-to-band and free exciton recombination is given. The decrease of  $B$  with increasing  $T$  is due to the decrease of the exciton concentration and of the Coulomb-enhancement of the band-to-band recombination rate. The latter however is smaller than the exciton recombination part even at room temperature. The constants of the exciton and band-to-band recombination are determined.

Es wurde die Temperaturabhängigkeit des Koeffizienten  $B$  der intrinsischen strahlenden Rekombination in Silizium von 100 bis 400 °K gemessen. Im Gegensatz zu früheren Rechnungen nimmt  $B$  mit der Temperatur ab. Zur Interpretation der Messungen wird eine einheitliche Theorie der indirekten strahlenden Band-Band- und Freien-Exzitonen-Rekombination aufgestellt. Die Abnahme von  $B$  mit steigendem  $T$  geht auf die Abnahme der Exzitonenkonzentration und der Coulomb-Vergrößerung der Band-Band-Rekombinationsrate zurück. Letztere ist jedoch noch bei Zimmertemperatur kleiner als der Exzitonenrekombinationsanteil. Die Konstanten der Exzitonen- und Band-Band-Rekombination werden bestimmt.

### 1. Introduction

Whereas the radiative band-to-band and free-exciton recombination in silicon is well known in its spectral distribution, especially at low temperatures [1 to 6], experimental results on the recombination cross-section or the radiative recombination coefficient (probability)  $B$  are sparse. In particular the temperature dependence of this quantity has not been determined experimentally in the past. Measurements of the temperature dependence of the photoluminescence spectrum, as given in [6] in the range 2 to 70 °K, do not include the recombination coefficient  $B$  as a function of  $T$ , because the exciting light intensity, but not the excess carrier concentration is kept constant in these experiments. Using the detailed balance theory of van Roosbroeck and Shockley [7], calculations from absorption spectra at different temperatures yielded a slight increase of  $B$  with  $T$  in silicon [3, 4]. In germanium, detailed balance calculations as well as measurements yielded a decrease of  $B$  with temperature [7, 8]. The latter is in contrast to theoretical expressions [9, 10], which contain the temperature dependence due to the participation of phonons, but which neglect

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the Coulomb attraction between electron and hole and therewith exciton recombination. A quantitative theory of the indirect radiative band-to-band and free-exciton recombination has not been carried out.

In this paper, measurements of the temperature dependence of the radiative recombination probability in silicon from 100 to 400 °K will be discussed. A theory of the radiative recombination is given, which takes into account exciton effects and which is in agreement with the obtained experimental results.

## 2. Experimental Method and Results

Using the method applied in [11, 12] at room temperature, the radiative recombination rate  $R$  was measured as a function of the injected electron and hole concentrations  $n$ ,  $p$  at different temperatures. Carriers were injected into the base region of a p-i-n device. Due to neutrality  $p = n$  and hence the recombination rate is

$$R = B n p = B n^2. \quad (1)$$

The radiative recombination probability  $B$  is then obtained as a function of temperature  $T$ .

The p-i-n rectifier was prepared by alloying and had a p-type base region with  $3 \times 10^{12}$  acceptors per  $\text{cm}^3$ . The high-level lifetime of the base region was  $10 \mu\text{s}$  at 300 °K, the thickness  $150 \mu\text{m}$  and the cross-section area  $1 \times 1 \text{ mm}^2$ . The sample was mounted on a copper plate and placed in a small vacuum chamber to enable a precise control of the temperature of the sample. The excess carriers were measured by extraction with a reverse voltage as described by Hoffmann and Schuster [13]. To extract rapidly enough so that the recombina-

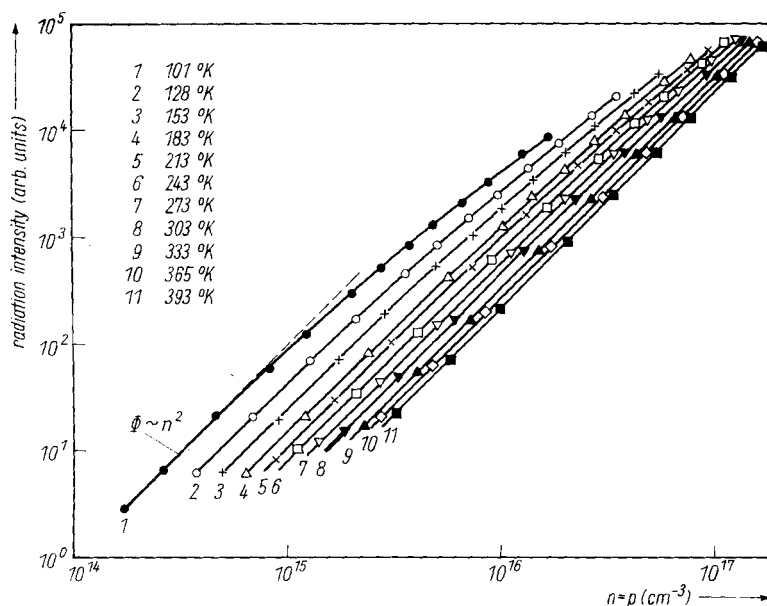


Fig. 1. Emitted radiation intensity as a function of injected carrier concentration at various temperatures

tion loss was negligible<sup>3</sup>), the vacuum chamber with the sample was inserted into a coaxial circuit. The concentration, which could be assumed homogeneous, was then obtained from

$$p = n = \frac{\int i_r(t) dt}{e V_i},$$

where  $i_r(t)$  is the reverse current at time  $t$ ,  $V$  the volume of the base region, and  $e$  the absolute electronic charge.

To obtain  $R$ , the radiation emerging parallel to the plane of the junctions was measured using a photomultiplier with S 1 characteristic. It was taken into account, that due to the variation of the spectral distribution of the radiation, the sensitivity of this detector depends on the temperature of the sample. The sensitivity variation with  $T$  was determined with a PbS cell.

In Fig. 1, the detected intensity  $\Phi$  at different temperatures is plotted on a logarithmic scale as a function of the injected concentration. At higher temperatures,  $\Phi$  is proportional to  $n^2$  in the entire range of concentrations. At lower temperatures, however, this is the case only at small concentrations (which however are still large compared with the doping concentration). The deviations from the quadratic law arise because a large fraction of the injected carriers form excitons which are included in the measured excess carrier concentration. Interpreting the deviation from  $n \sim (\text{intensity})^{1/2}$  as exciton concentration, the thermal binding energy of the free excitons can be determined [31]. In the present paper we consider that part of Fig. 1 where  $\Phi \sim n^2$ .<sup>4</sup>)

As is seen, the radiation at a given concentration, and therefore  $B$ , decreases with increasing  $T$ . To obtain the accurate  $B(T)$  dependence, the emitted intensity must be corrected for reabsorption at higher temperatures. The mean absorption coefficient  $\alpha$  used for this purpose in the expression (4) of [11], is shown

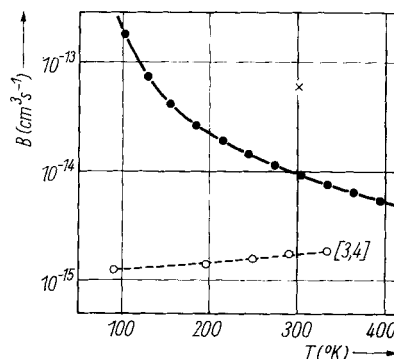


Fig. 2. Radiative recombination probability  $B$  as a function of temperature. The full curve is obtained from Fig. 1 by taking into account reabsorption.  $\circ$  Points calculated by Varshni [3] and Michaelis and Pilkuhn [4] from absorption spectra.  $\times$  Experimental value of Blinov et al. [17]

<sup>3</sup>) As is to be appended, the loss in extracted carriers by recombination is normally smaller than calculated from the mean lifetime in the base region. This is because the recombination during the extraction takes place mainly in the interior of the base [14], where the lifetime is usually larger than near the highly doped end regions. Recombination in the  $p^+$ - and  $n^+$ -region themselves [15] is suppressed the more.

<sup>4</sup>) Krausse [12] observes a strong deviation from  $\Phi \sim n^2$  for  $n \gtrsim 5 \times 10^{16} \text{ cm}^{-3}$  even at room temperature. We find with the samples left kindly to us by Dr. Krausse, no or even very small deviations from the quadratic relationship for  $n \lesssim 2 \times 10^{17} \text{ cm}^{-3}$  at 300 °K. The cause of these differences arising from the experimental equipments has not been located till now.

in Table 1 for the different temperatures. Using further at 300 °K the absolute value  $B = 0.95 \times 10^{-14} \text{ cm}^3/\text{s}$ ,<sup>5)</sup> the  $B(T)$  dependence shown in Fig. 2 is obtained.  $B$  decreases by a factor of about 30 in the range 100 to 400 °K. We will now compare these measurements with results obtained from absorption spectra and then give a physical theory.

Table 1

Mean absorption coefficient  $\alpha$  of the recombination radiation as a function of temperature.  $\alpha$  was determined experimentally for the different temperatures using diodes with varying rectangular cross-sections. The intensity of the radiation emerging from the different sample depths was observed with a PbS cell (see footnote<sup>5)</sup>)

$T$ (°K)	$\alpha$ (cm <sup>-1</sup> )
101	0.63
128	0.83
153	1.0
183	1.3
213	1.6
243	1.9
273	2.3
303	2.7
333	3.2
363	3.8
393	4.6

### 3. Comparison with Calculations from Absorption Data

Detailed balance calculations [7] using the absorption spectra of MacFarlane et al. [16] were carried out by Varshni [3] and Michaelis and Pilkuhn [4]. The results of these authors are shown also in Fig. 2. As is seen, the calculated  $B$  increases slightly with  $T$  and is also smaller than the experimental value, at 100 °K for example by a factor of about 100. The experimental value of Blinov et al. [17] at 300 °K is larger than our result. An increase of  $B$  with  $T$  now is not only in contradiction with reported measurements but also with the theory given in the next section. The erroneous results of the van Roosbroeck-Shockley calculations may be caused by the fact that the main part of the recombination rate arises from the absorption branch due to absorption of phonons which is small and experimentally widely undetermined at lower temperatures. More accurate values of the recombination probability should be calculated after transforming the experimental absorption spectra owing to emission of phonons to the needed optical absorption spectra associated with absorption of phonons [2].

### 4. Theory

Dumke [9] and Hall [10] (see also [3]) obtained for the coefficient of the indirect radiative band-to-band recombination of free electrons and holes with participation of phonons of a single type

$$B_0 = \frac{4 \pi \epsilon \hbar^3 E_g^2 A}{c^2 (m_{de} m_{dh})^{3/2}} \frac{e^{\theta/T} + 1}{e^{\theta/T} - 1} \equiv C \frac{e^{\theta/T} + 1}{e^{\theta/T} - 1}. \quad (2)$$

<sup>5)</sup> The  $B$ -value given in [11] was corrected within the limits of accuracy using for the average absorption coefficient at 300 °K the value  $\alpha = 2.7 \text{ cm}^{-1}$  (see Table 1) instead of  $5 \text{ cm}^{-1}$ . The absorption coefficient  $5 \text{ cm}^{-1}$  is obtained with a photomultiplier, but this value is too large due to the higher sensitivity of the S1 characteristic at the stronger absorbed high-energy side of the emission spectrum. A mean absorption of  $3 \text{ cm}^{-1}$  was determined in [4].

In (2),  $k\theta$  is the energy of the phonons with wave vector  $\mathbf{k}_c$  of the conduction band minimum,  $m_{de}$  and  $m_{dh}$  are the density-of-states effective masses of electrons and holes, respectively,  $E_g$  is the energy gap,  $\epsilon$  the dielectric constant, and  $A$  a quantity occurring also in corresponding expressions for absorption [18, 19],  $A$  and  $C$  may be assumed to a first approximation as constants. Owing to the increase of the phonon emission and absorption probability,  $B_0$  increases with temperature. In silicon, the intrinsic radiative recombination is to the main part due to the participation of transverse optical phonons with  $\theta = 670^\circ\text{K}$  [2, 3].

The  $B_0$ -quantity of (2) would be equal to the real recombination probability  $B$ , if the Coulomb attraction between electron and hole were negligible. But causing exciton recombination and also a strong enhancement of the band-to-band recombination rate, Coulomb interaction constitutes a dominating factor in the recombination process. A theory of the radiative recombination including the Coulomb interaction is given in this section, in doing so advantage will be taken of the analogous theory of exciton absorption [20, 21].

The Coulomb attraction enhances the probability that an electron and hole can be found at the same position, say at their centre of mass. This probability is given by the product of the expectation values of the electron and hole concentrations at the centre of mass of the pairs in a given state  $s$ , which product will be denoted by  $n_s(0)p_s$ . In a less symmetrical formulation, this is the product of the electron concentration at the position of holes,  $n_s(0)$ , and the hole concentration  $p_s$ .  $n_s(0)p_s$  is larger than the product of the mean concentrations  $n_s p_s$  by a factor which depends on the two-particle state  $s$ . Equation (2) now is obtained on the assumption that the recombination rate  $R_s$  as a function of  $s$  is simply proportional to  $n_s p_s$ . With inclusion of Coulomb attraction

$$R_s = B_0 n_s(0)p_s. \quad (3)$$

The internal recombination probability  $B_0$  relating to electrons and holes "at the same point" is assumed to be the same for all states *including the excitons*.<sup>6)</sup> This is a suitable approximation if the energies of all electron-hole pairs are nearly equal ( $\approx E_g$ ), as is the case in semiconductors like silicon up to high temperatures. For indirect transitions with emission and absorption of phonons,  $B_0$  is given by (2). Introducing the radial solution  $\Phi_s(r)$  of the hydrogen-like Schrödinger equation of the electron-hole system in the usual normalization [20 to 23], we have

$$n_s(0)p_s = |\Phi_s(0)|^2 n_s p_s \quad (4)$$

for unbound states, and

$$n_s(0)p_s = |\Phi_s(0)|^2 n_{es} \quad (5)$$

for exciton states. In the latter case, the concentration of electrons at the positions of holes is independent of the exciton concentration  $n_{es} \equiv n_s = p_s$ . The integral recombination rate is

$$\begin{aligned} R &= B_0 \sum_s n_s(0) p_s = \\ &= B_0 \left( \sum_{\text{band states}} |\Phi_s(0)|^2 n_s p_s + \sum_{\text{exciton states}} |\Phi_s(0)|^2 n_{es} \right). \end{aligned} \quad (6)$$

<sup>6)</sup> To avoid unessential complications arising from the different recombination behaviour of the spin states,  $B_0$  is defined as the average value over the four spin states belonging to one external state of the pair. If spin is exactly conserved,  $B_0$  is 1/4 of the value owing to electron-hole pairs with spin zero.

For the explicit evaluation, we consider the case of two non-degenerate spherical bands with effective masses  $m_e$  and  $m_h$ . The minimum of the conduction band may be displaced by a wave vector  $\mathbf{k}_c$  from the valence band maximum at  $\mathbf{k} = 0$ . With  $\mathbf{k}_e$ ,  $\mathbf{k}_h$  denoting the wave vectors of free electrons and holes, modified wave vectors of the centre-of-mass system are defined by

$$\mathbf{K} \equiv \mathbf{k}_e - \mathbf{k}_c + \mathbf{k}_h, \\ \mathbf{k} \equiv \frac{m_h}{m_e + m_h} (\mathbf{k}_e - \mathbf{k}_c) - \frac{m_e}{m_e + m_h} \mathbf{k}_h, \quad (7)$$

where  $\hbar \mathbf{K}$ ,  $\hbar \mathbf{k}$  apart from additive constants are equal to the momenta conjugate to the centre-of-mass coordinate and to the relative coordinate  $\mathbf{r}_e - \mathbf{r}_h$ , respectively. The energy of an unbound electron-hole pair can be written

$$E = E_g + \frac{\hbar^2 (\mathbf{k}_e - \mathbf{k}_c)^2}{2 m_e} + \frac{\hbar^2 \mathbf{k}^2}{2 m_h} = E_g + \frac{\hbar^2 \mathbf{K}^2}{2 M} + \frac{\hbar^2 \mathbf{k}^2}{2 \mu} \quad (8)$$

( $M = m_e + m_h$ ,  $\mu = m_e m_h / (m_e + m_h)$ ). For a state with relative energy  $E_r \equiv \hbar^2 \mathbf{k}^2 / 2 \mu$ , the quantum mechanical probability  $|\Phi_s(0)|^2 = |\Phi_{\mathbf{k}}(0)|^2$  of finding an electron and a hole at the same point is given by [20, 21]

$$|\Phi_{\mathbf{k}}(0)|^2 = \frac{\pi \sqrt{G/E_r} \exp(\pi \sqrt{G/E_r})}{\sinh(\pi \sqrt{G/E_r})} \approx 2 \pi \sqrt{\frac{G}{E_r(\mathbf{k})}}, \quad (9)$$

where  $G \equiv \mu e^4 / (2 \hbar^2 \epsilon^2)$  is the exciton Rydberg. The approximation on the right-hand side of (9) is valid for small  $E_r$ , but can be used in the integration (13) up to high temperatures in silicon ( $kT \ll 4 \pi^2 G$ ). For the exciton states,  $|\Phi_s(0)|^2 = |\Phi_{n_q}(0)|^2$  ( $n_q$  total quantum number) is non-zero only for s states and then

$$|\Phi_{n_q}(0)|^2 = \frac{1}{\pi a^3 n_q^3}, \quad a \equiv \frac{\hbar^2 \epsilon}{\mu e^2}. \quad (10)$$

Using Boltzmann statistics and replacing the summation over band states in (6) by integration, the sum terms become differentials according to

$$n_s p_s \rightarrow n p \cdot \frac{e^{-\left(\frac{\hbar^2 \mathbf{K}^2}{2 M} + \frac{\hbar^2 \mathbf{k}^2}{2 \mu}\right)/kT}}{(2 \pi)^3} \frac{2}{(2 \pi)^3} d^3 \mathbf{K} \frac{2}{(2 \pi)^3} d^3 \mathbf{k} \\ \frac{2}{(2 \pi)^3} \int e^{-\frac{\hbar^2 \mathbf{K}^2}{2 M}/kT} d^3 \mathbf{K} \frac{2}{(2 \pi)^3} \int e^{-\frac{\hbar^2 \mathbf{k}^2}{2 \mu}/kT} d^3 \mathbf{k} \quad (11)$$

$$n_{es} \rightarrow n p \cdot \frac{e^{-\left(\frac{\hbar^2 \mathbf{K}^2}{2 M} - \frac{G}{n_q}\right)/kT}}{(2 \pi)^3} \frac{4}{(2 \pi)^3} d^3 \mathbf{K} \\ \frac{2}{(2 \pi)^3} \int e^{-\frac{\hbar^2 \mathbf{K}^2}{2 M}/kT} d^3 \mathbf{K} \frac{2}{(2 \pi)^3} \int e^{-\frac{\hbar^2 \mathbf{k}^2}{2 \mu}/kT} d^3 \mathbf{k} \quad (12)$$

Integration over the right-hand side of (11) yields  $n p$ , showing the correct choice of the normalization factor. The same factor, however, applies also to the occupation of exciton states (12) in thermal equilibrium with the free carriers [24]. For each external state, two spin states for a single carrier and four spin states for an exciton have been taken into account. Considering  $N$  conduction band minima at equivalent wave vectors  $\mathbf{k}_{ci}$ ,  $N$  appears in the numerators and denomi-

nators of (11), (12) and drops out. Inserting now (9) to (12) into (6), one obtains

$$R = \frac{B_0 n p}{(2\pi)^3} \int e^{-\frac{\hbar^2 \mathbf{k}^2}{2\mu}/kT} d^3\mathbf{k} \times \left\{ \frac{4\pi}{(2\pi)^3} \int \sqrt{\frac{G}{\hbar^2 \mathbf{k}^2/2\mu}} e^{-\frac{\hbar^2 \mathbf{k}^2}{2\mu}/kT} d^3\mathbf{k} + \sum_{n_q=1}^{\infty} \frac{2}{\pi a^3 n_q^3} e^{G/(n_q^2 kT)} \right\}. \quad (13)$$

Equation (13) yields for the recombination coefficient

$$B = 4\sqrt{\pi} \sqrt{\frac{G}{kT}} \left( 1 + 2 \frac{G}{kT} \sum_{n_q=1}^{\infty} \frac{\exp \frac{G}{n_q^2 kT}}{n_q^3} \right) \coth \left( \frac{\theta}{2T} \right) C, \quad (14)$$

where already (2) has been inserted. In a good approximation  $B$  is given by

$$B = 4\sqrt{\pi} \sqrt{\frac{G}{kT}} \left( 1 + 2 \frac{G}{kT} e^{G/kT} \right) \coth \left( \frac{\theta}{2T} \right) C. \quad (15)$$

The 1 in the bracket of (14) and (15) corresponds to the band-to-band recombination, the second term to the exciton recombination. The band-to-band recombination probability is enhanced by the factor  $4\sqrt{\pi} \sqrt{G/kT}$  compared with the case of absent Coulomb attraction (equation (2)). The ratio of the exciton to the band-to-band recombination probability is

$$\frac{B_e}{B_{bb}} = 2 \frac{G}{kT} \sum_{n_q=1}^{\infty} \frac{1}{n_q^3} e^{G/(n_q^2 kT)} \approx 2 \frac{G}{kT} e^{G/kT}. \quad (16)$$

According to  $R_e = B_e n p = n_e/\tau_e$ ,  $B_e$  contains the exciton concentration  $n_e$  and the exciton lifetime  $\tau_e$ . Considering excitons in the ground state only, one has

$$n_e = n p \left( \frac{\hbar^2}{2\pi\mu kT} \right)^{3/2} \exp \frac{G}{kT}. \quad (17)$$

Equations (6) and (10) with  $n = 1$  yield

$$\tau_e = \frac{\pi a^3}{B_0} = \frac{\pi}{C} \left( \frac{\hbar^2 \epsilon}{\mu e^2} \right)^3 \tanh \frac{\theta}{2T}. \quad (18)$$

Equations (14) to (16) can be obtained also by inserting the absorption expressions of Elliott [20] and McLean [21] into the detailed balance equation of van Roosbroeck and Shockley [7]. But this indirect derivation is algebraically lengthy and furthermore would be less suited for understanding the recombination process physically.

## 5. Discussion

Equation (14) yields in agreement with the measurements a decrease of  $B$  with  $T$ , except for a range of high temperatures, where the increase of the coth-factor from phonon participation predominates. The decrease of  $B$  with temperature is essentially due to the decrease of the exciton recombination part given by (16) to (18), and also to the reduction of Coulomb enhancement of the band-to-band recombination.

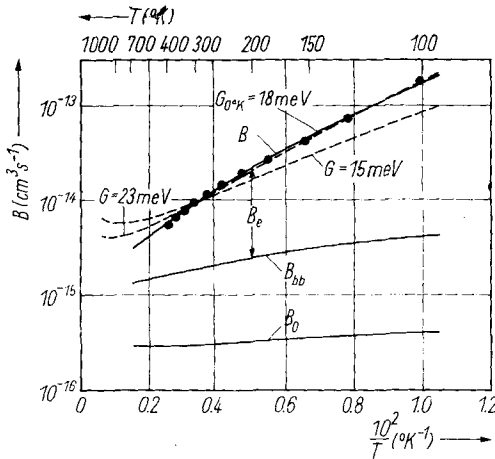


Fig. 3. Interpretation of measurements. The full theoretical curves for  $B$ ,  $B_{bb}$ , and  $B_0$  were obtained from (14), (16), and (2) with variable  $G$  and  $C$  using  $G = 18$  meV at 0 °K and  $A = 690$  cm<sup>-1</sup> eV<sup>-2</sup>. ● Experimental points; — — — theory with constant  $G$  and  $C$

A detailed comparison between theory and experiment is given in Fig. 3 where the radiative recombination coefficient has been plotted as a function of  $1/T$ . In the theoretical curves, a  $\theta$ -value of 670 °K for the transverse optical phonons was used. The binding energy of free excitons in silicon was calculated by McLean and Loudon [25], who obtained  $G = 14$  meV with the band parameters at 4 °K. From the absorption spectrum at 2 °K, Shaklee and Nahory [26] determined a  $G$ -value of 15 meV, which was confirmed also by other measurements [27]. As can be seen from Fig. 3, the theoretical curve for  $G = 15$  meV and a  $C$ -value obtained by fitting at 300 °K shows a slope which is too small. A good fit to the experimental points below room temperature is obtained with  $G = 23$  meV, but at higher temperatures the slope of this curve is too small also. For a more accurate interpretation it is not justified to assume the quantity  $C$  and the binding energy  $G$  temperature-independent. Due to the decrease of the energy gap and the increase of the effective masses with  $T$  [21, 28 to 30],  $C$  decreases remarkably with  $T$ , if, as in earlier papers, the quantity  $A$  in (2) is assumed constant. Within the theory of Section 4, the binding energy  $G$  is proportional to

$$\mu(T) = \frac{m_{de}(T)/M_c^{2/3} m_{dh}(T)}{m_{de}(T)/M_c^{2/3} + m_{dh}(T)}$$

( $M_c = 6$  is the number of equivalent conduction band minima), and hence increases slightly with  $T$ . With the temperature dependence of  $C$  and  $G$ , obtained from  $m_{de}(T)$ ,  $m_{dh}(T)$  given by Barber [29], good agreement with the measurements is obtained in the whole temperature range, if a binding energy of 18 meV at low temperatures is used (thick full curve).  $C$  decreases then by a factor 2.4, whereas  $G$  increases by nearly 25% in the range 0 to 400 °K.

As is seen, the temperature dependence of  $B$  suggests that the binding energy of free excitons in silicon is somewhat larger than the spectroscopically found value of 15 meV. This is supported by evaluating the deviations from the law  $n \sim (\text{intensity})^{1/2}$  in Fig. 1 (see Section 2) by use of (17), which leads to a thermal binding energy of  $\approx 23$  meV at 115 °K [31]. The discrepancies however should not be overvalued. Apart from experimental uncertainties, the theory used in this paper as well as in [20, 26, 27], neglects degeneracy, split up band, and aniso-



tropy. Further, because it is not confirmed that the factor  $A$  in (2) is constant to a sufficient extent, the experimental  $B(T)$  can be fitted also at somewhat differing  $G$ -values with a slightly temperature-dependent  $A$ .

The value of  $A$  obtained from the absolute magnitude of  $B$  in the curve with  $G_{0^\circ\text{K}} = 18 \text{ meV}$ , amounts to  $690 \text{ cm}^{-1} \text{ eV}^{-2}$ . From the absorption spectrum, Hall [10] determined  $A = 3600 \text{ cm}^{-1} \text{ eV}^{-2}$  and Varshni [3]  $A = 2682 \text{ cm}^{-1} \text{ eV}^{-2}$ . These values should be too high, because the measured absorption was totally attributed to band-to-band transitions of non-interacting carriers, and hence the Coulomb enhancement of band-to-band absorption as well as absorption into exciton states was projected into the quantity  $A$ .

For comparison, we have plotted in Fig. 3 also the recombination probability  $B_0$  for negligible Coulomb interaction and the band-to-band recombination probability  $B_{bb}$  with inclusion of the Coulomb attraction, referring to the full curve for  $B$ . It is seen, that the enhancement of the band-to-band recombination coefficient by Coulomb attraction,  $B_{bb} - B_0$ , is very strong. As is noticeable further, the exciton recombination probability  $B_e = B - B_{bb}$  is larger than  $B_{bb}$  even at room temperature, although only a small fraction of carriers is bound in exciton states. This is because the radiative lifetime due to band-to-band transitions,  $\tau_{bb}$ , is much larger than the radiative lifetime of the excitons. For  $n = 10^{16} \text{ cm}^{-3}$  and  $300^\circ\text{K}$ , one obtains from Fig. 3: total radiative lifetime  $\tau = 1/(Bn) = 10 \text{ ms}$  and  $\tau_{bb} = 1/(B_{bb}n) = 52 \text{ ms}$ . For the exciton lifetime, insertion of  $C = 2.4 \times 10^{-16} \text{ cm}^3/\text{s}$  (obtained at  $300^\circ\text{K}$  from the determined  $A$ -value) and a reduced effective mass of  $0.25 m_0$  into (18) yields

$$\tau_e = 210 \tanh \frac{\theta}{2T} \quad \mu\text{s}.$$

The exact agreement with [5], where a free-exciton lifetime of  $200 \mu\text{s}$  was estimated at low temperatures, may be to some extent fortuitous.

As is to be mentioned, a limitation of the theory results from the neglect of many-particle Coulomb effects. Concentrations where screening of the Coulomb attraction [32] and band shrinkage become significant [33], exceed the range covered by the measurements.

Since the experimental points are well reproduced by the theoretical curve the latter can be used for an extrapolation to higher temperatures, where the experimental method is no longer applicable on account of too large reverse currents in the p-n junction. The obtained results, including the temperature dependence of reabsorption, form the basis for the use of the recombination radiation in temperature-dependent device investigations.

## Appendix

### *Spectral distribution of the radiation*

As well as the integral recombination coefficient, the spectral distribution of the indirect radiative band-to-band and exciton recombination has not been given theoretically in previous papers. Hence its general significance calls for the inclusion of the emission spectrum as obtained from Section 4. For this purpose, the recombination parts owing to the emission and absorption of phonons of a certain type must be treated separately. Referring in the formulation to the case of phonon emission the combined recombination coefficient  $B_0$

has to be replaced by

$$B_{0e} = B_0 \frac{e^{\theta/T}}{e^{\theta/T} + 1} = C \frac{e^{\theta/T}}{e^{\theta/T} - 1}. \quad (A1)$$

The number of emitted photons of energy  $\hbar \nu$  is then obtained by integrating (3) over those two-particle states which have energy  $E = \hbar \nu + k \theta$ . Multiplying (3) by  $\delta(\hbar \nu + k \theta - E)$ , where  $E = E_g + (\hbar^2 \mathbf{k}^2/2\mu) + (\hbar^2 \mathbf{K}^2/2M)$  for unbound states and  $E = E_g - (G/n_q^2) + (\hbar^2 \mathbf{K}^2/2M)$  for exciton states, and using (4), (5), and (9) to (12), integration yields

$$\begin{aligned} R_{\nu e} d\frac{\hbar \nu}{kT} &= n p \frac{16 C e^{\theta/T}}{e^{\theta/T} - 1} \sqrt{\frac{G}{kT}} \times \\ &\times \operatorname{Re} \left\{ \frac{G}{kT} \sum_{n_q=1}^{\infty} \frac{1}{n_q^3} \sqrt{\frac{\hbar \nu + k \theta - E_g + G/n_q^2}{kT}} + \frac{1}{3} \left( \frac{\hbar \nu + k \theta - E_g}{kT} \right)^{3/2} \right\} \times \\ &\times e^{-(\hbar \nu + k \theta - E_g)/kT} d\frac{\hbar \nu}{kT}, \end{aligned} \quad (A2)$$

where  $R_{\nu e}$  denotes the recombination rate at frequency  $\nu$  for phonon emission. Formation of the real part means that for negative arguments the contributions of the 1/2 and 3/2 power terms are zero. The spectrum for phonon absorption is the same except that  $k \theta$  is replaced by  $-k \theta$  and  $B_{0e}$  by  $B_{0a} = B_{0e} e^{-\theta/T}$ .

With (A2), we have calculated the combined radiation spectrum of the indirect band-to-band and free-exciton recombination. The series term corresponds to recombination from exciton states, the second term represents the band-to-band spectrum. In spite of the different onset energies, a separation of both recombination parts with corresponding extrema in the total spectrum is not obtained for any  $G/kT$ . The distribution has a maximum at about  $E_g - k \theta$  and is in general agreement with experimental results [1 to 4], which on the base of this theory can be evaluated more quantitatively. As is to be mentioned, recombination from the first excited exciton s-state ( $n_q = 2$ ) produces a previously not indicated peak which one should be able to observe or  $G/kT$  not strongly differing from unity.

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