

Band-gap narrowing in heavily doped silicon at 20 and 300 K studied by photoluminescence

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The band-gap shrinkage in heavily doped *n*- and *p*-type silicon is studied by photoluminescence both at low temperatures (20 K) and at room temperature (300 K). A line-shape analysis was performed to determine the indirect band-gap energy from the emission spectra. Within the experimental accuracy the same band-gap shift is observed at room temperature as at low temperature. The present results are compared with experimental data from other optical studies and with theoretical calculations.

The band-gap narrowing in heavily doped silicon is of basic as well as practical interest, e.g., for the modeling of device properties.¹ Quantitative data on this band-gap narrowing have been derived from electrical-transport experiments² as well as from optical measurements like absorption³⁻⁵ and photoluminescence (PL).⁶⁻⁹

The determination of the band-gap shift from transport measurements, however, depends very much on the model used for the evaluation of the data.¹⁰ Therefore this method does not provide a useful tool to determine the band-gap shrinkage upon doping accurately. Optical absorption is a more direct way to measure the band-gap energy as a function of the carrier concentration. In silicon, however, the band-to-band absorption spectrum overlaps strongly with the free-carrier absorption for photon energies close to the band-gap energy. Therefore one has to rely on the extrapolation of the absorption spectrum at photon energies high above the band gap to zero absorption to determine the band-gap energy. The band-gap shrinkage obtained by this method is up to 50 meV smaller than the shrinkage determined by transport measurements^{7,8,11} or photoluminescence experiments.^{7,8,9} As pointed out by Dumke,⁷ this discrepancy can be caused by a nonrigid shift of the bands which is greater for states close to the band edges than for states higher up in energy.

The photoluminescence (PL) technique has been proven as a reliable tool to measure the band-gap shift in heavily doped silicon.⁶⁻⁹ This technique measures the spectrum emitted by the radiative recombination of photo-created minority carriers. The emission band extends from the reduced band-gap energy $E_{G,2}$ (low-energy edge), which is the difference between the top of the valence band and the bottom of conduction band, to the energy of the optical gap $E_{G,1}$ (high-energy cutoff), which is the sum of $E_{G,2}$ and the band filling E_F .

Using the related technique of photoluminescence excitation (PLE) spectroscopy, which allows to "see through" the free-carrier absorption, the indirect absorption edge could be measured directly in heavily doped silicon.^{9,12} The band-gap reduction obtained by this technique is in good agreement with the data from photoluminescence measurements. This finding gives further confidence in the band-gap shifts determined by the photoluminescence technique.

In the present study, data on the band-gap narrowing upon doping are presented both for low temperatures and for room temperature. Previous studies for dopant concentrations above $4 \times 10^{19} \text{ cm}^{-3}$ were only restricted to the

low-temperature range ($\leq 20 \text{ K}$).^{6-9,12} For dopant densities below that value, temperature-dependent PL studies ($\leq 160 \text{ K}$) are reported for *n*-type silicon in the literature.^{13,14} However, room-temperature data up to doping levels of $\geq 10^{20} \text{ cm}^{-3}$ for *n*- and *p*-type material are of great interest for the device application.

The samples used in the present study were bulk doped with a maximum carrier concentration of $1.5 \times 10^{20} \text{ cm}^{-3}$ for *n*-type and $4 \times 10^{20} \text{ cm}^{-3}$ for *p*-type material. They were mounted in a temperature-controlled cryostat and the luminescence was excited by the 647 nm line of a Kr^+ laser at a power density of 200–400 W/cm^2 . The luminescence light was dispersed with a 1-m double monochromator and detected with an intrinsic Ge photodiode.

In a previous study,⁹ the shrinkage of the reduced band gap $E_{G,2}$ was determined from low-temperature PL spectra, taking the point on the low-energy side of the emission band, where the intensity is 5% of the peak value, to define $E_{G,2}$. To get a more objective measure for $E_{G,2}$, the PL spectra presented in Ref. 9 were reanalyzed performing a line-shape analysis.¹² The emission line shape $I(h\nu)$ was expressed, assuming constant matrix elements, by the convolution of the densities of states $D_e(E)$ and $D_h(E)$ weighted by the distribution functions $f_e(E)$ and $f_h(E)$ (the subscripts *e* and *h* stand for electrons and holes, respectively).^{12,15}

$$I(h\nu) \sim \int_0^\infty f_e(E) D_e(E) f_h(h\nu - E_{G,2} - E) \times D_h(h\nu - E_{G,2} - E) dE \quad (1)$$

For *n*-type [*p*-type] doping $f_e(E)$ [$f_h(E)$] represents the Fermi distribution function and $f_h(E)$ [$f_e(E)$] can be described by a Boltzmann distribution. Thereby, thermalization of the minority carriers is assumed. For *n*-type material a parabolic conduction band was used for calculating $D_e(E)$, whereas for *p*-type material the complex structure of the valence band was taken into account.¹⁶ To include band-tailing effects, incomplete thermalization of the carriers and the finite resolution in the experiment, a Gaussian broadening of $I(h\nu)$ was introduced^{7,12} with a broadening parameter E_S . For details of the fitting procedure see Ref. 12.

The shift ΔE_G of the reduced band gap $E_{G,2}$ with respect to the band gap of pure silicon E_G (pure), as obtained from the line-shape analysis, is plotted versus carrier concentration in Fig. 1. Also shown are experimental PL data for *n*-

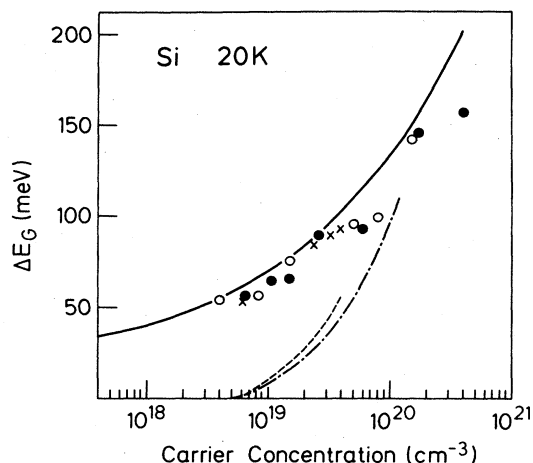


FIG. 1. Shift of the reduced band gap $\Delta E_G = E_G(\text{pure}) - E_{G,2}$ [$E_G(\text{pure}) = 1.17$ eV] vs carrier concentration at 20 K. The open (*n*-type) and filled (*p*-type) circles show data from the present study and the crosses are data for *n*-type doping from Dumke (Ref. 7). The solid line refers to the calculation by Berggren and Sernelius (Ref. 17) assuming a random arrangement of the donors. The dashed (*n*-type) and dash-dotted (*p*-type) curves give the results of low-temperature absorption measurements by Schmid (Ref. 5).

type material reported by Dumke, which were also obtained by a line-shape analysis.⁷ They are, within the experimental error, in good agreement with the present data. For comparison, the results of absorption measurements by Schmid⁵ and of theoretical calculations by Berggren and Sernelius¹⁷ are also depicted.

In order to determine the band-gap shrinkage upon doping at 300 K, PL spectra were recorded also at room temperature. Two examples for Si:B, 1.7×10^{20} carriers/cm³, and Si:P, 8×10^{19} carriers/cm³ are shown in Fig. 2. Again, a line-shape analysis was performed to deduce $E_{G,2}$ from the experimental spectra. As for calculating the low-temperature spectra, Eq. (1) was used to compute the room-temperature spectra. To account for the various Stokes and anti-Stokes phonon replicas up to seven calculated curves were superimposed—Stokes and anti-Stokes replica of the three phonon-assisted emission lines plus, for *n*-type doping, the no-phonon replica. The relative coupling strengths of the various replicas were taken from the low-temperature line-shape analysis.¹² The intensity ratio of the anti-Stokes and the Stokes component of each particular phonon replica was calculated using Bose-Einstein distribution factors.

For *n*-type samples, the chemical potential μ was calculated from the known carrier concentration n by inverting the following expression:¹⁸

$$n = N_c F_{1/2}(\mu/k_B T) \quad (2)$$

N_c denotes the effective density of states in the conduction band, $F_{1/2}$ the Fermi integral, and T the temperature of the electrons. For *n*-type silicon at room temperature [electron density-of-states mass $m_{de} = 1.062 m_0$ (Ref. 19)] the effective density of states amounts to $N_c = 3.1 \times 10^{19}$ cm⁻³.¹⁸ The carrier temperature used for the line-shape calculations was 300–330 K. The only remaining fitting parameters are the reduced band gap $E_{G,2}$ and the broadening E_S .

For *p*-type samples the calculation of the chemical poten-

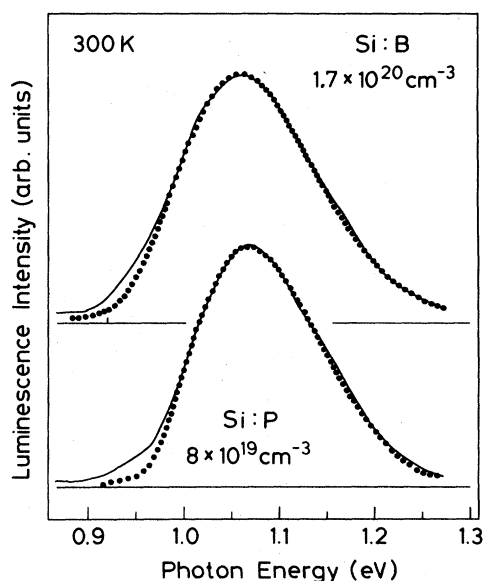


FIG. 2. Room-temperature PL spectra (solid line) for Si:P (8×10^{19} carriers/cm³) and Si:B (1.7×10^{20} carriers/cm³). The dotted curves show calculated emission line shapes fitted to the experimental spectra (see text).

tial for a given carrier concentration is not as straightforward as for *n*-type doping due to the complex structure of the valence band.¹⁶ Therefore $E_{G,2}$, E_S , and the chemical potential μ were used as fitting parameters. The values of μ derived from the line-shape fit are comparable to the chemical potential which was estimated assuming a parabolic valence band with a carrier-density-dependent hole density-of-states mass.¹⁶

The best fits obtained are also shown in Fig. 2. The agreement between the experimental and the fitted curve is good except for the low-energy edge. But as discussed for the low-temperature spectra,¹² this might be due to the simple way used to include band-tailing effects in the present line-shape calculations. For the same reason, the present line-shape model failed to give a satisfactory fit to the low-energy side of the experimental spectra for carrier concentrations below the degeneracy limit [$\approx (2-3) \times 10^{19}$ cm⁻³ at 300 K (Ref. 18)]. Therefore, the point on the low-energy side at which the luminescence intensity is 10% of the peak value has been used to define $E_{G,2}$ for samples with carrier concentrations in the range of 10^{18} – 10^{19} cm⁻³. This choice is justified by the fact that, for carrier concentrations above the degeneracy limit, the 10% point coincides within a few meV with the position of $E_{G,2}$ deduced from the line-shape analysis.

The shift of the reduced band gap $E_{G,2}$ relative to the gap of pure silicon obtained from the analysis described above, is plotted in Fig. 3 versus the carrier concentration together with the room-temperature absorption data on *n*-type silicon reported by Balkanski, Aziza, and Amzallag,⁴ and theoretical calculations for *n*-type silicon at 300 K by Saunderson.²⁰ Also at room temperature the band-gap shrinkage obtained from absorption measurements^{4,5} is smaller than the shrinkage determined by PL experiments. That discrepancy is of the same order (≤ 50 meV) as for low temperatures.^{7,9}

Comparing the band-gap energies at 20 and 300 K, within

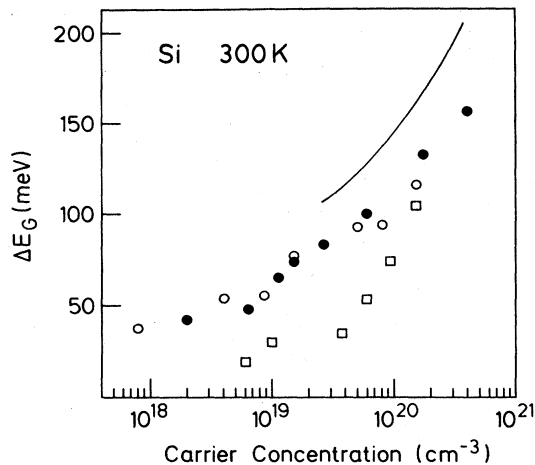


FIG. 3. Shift of the reduced band gap $\Delta E_G = E_G(\text{pure}) - E_{G,2}$ [$E_G(\text{pure}) = 1.11$ eV] vs carrier concentration at 300 K. The open (n -type) and filled (p -type) circles show data from the present study. The open squares represent absorption data from Balkanski *et al.* (Ref. 4). The solid line refers to the calculation of the room-temperature band-gap shrinkage in n -type silicon by Saunderson (Ref. 20).

the experimental error, the same gap shrinkage is observed. This result is consistent with the absorption data by Balkanski *et al.*⁴ and Schmid.⁵ They find, within a few meV, the same band-gap narrowing at low temperature as at room temperature.²¹ Judging from the scatter of the PL data, the accuracy of the present results can be estimated to about ± 10 meV. Improvements on that point could be obtained by using a more detailed model for band-tailing effects in

the calculation of the emission line shape. Another effect, which should be included in a future study, is the additional broadening due to the finite lifetime in the final state of the luminescence transition.^{22,23}

The result of recent calculations by Berggren and Sernelius,¹⁷ performed for n -type doping and zero temperature, gives a good description of the present low-temperature data (see Fig. 1). Calculations of the band-gap reduction in n -type as well as p -type silicon for zero temperature have been carried out by Abram, Childs, and Saunderson.²⁴ Their results (not shown in Fig. 1) are in good agreement with the calculations by Berggren and Sernelius.¹⁷ The agreement of the room-temperature calculations by Saunderson²⁰ with the present experimental data (see Fig. 3), however, is less satisfactory than for the low-temperature case discussed above. Over the whole range covered by the theory the experimental gap shrinkage is smaller than the reduction predicted by theory.

In summary, the narrowing of the band gap with doping has been studied by PL spectroscopy at low temperatures (20 K) and at room temperature (300 K). To extract the energy of the reduced band gap from the experimental spectra a line-shape analysis has been performed. The shrinkage of the reduced band gap, with respect to the band gap of pure material, is found to be the same, within the experimental error, at 300 as at 20 K. The gap reduction is also independent on the type of doping (n or p type).

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