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Ultralow Values of the Absorption Coefficient of Si Obtained from Luminescence

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Photoluminescence spectra were measured on homogeneously doped silicon at temperatures of 90 and 295 K. By using the generalized Planck law for the emission of luminescence by indirect transitions, values for the absorption coefficient as small as 10^{-16} cm^{-1} have been obtained for photon energies well below the band gap. At higher photon energies, where absorption coefficients can be obtained from transmission, good agreement with literature data is observed.

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Photon emission by luminescence via direct transitions is described by a generalized Planck emission law with a nonzero chemical potential μ_γ of the emitted photons as the only parameter, which distinguishes luminescence from pure thermal radiation, for which $\mu_\gamma = 0$ [1,2]. Although luminescence from indirect transitions in germanium has been calculated in an approximate way even earlier than for direct transitions [3], it has been proven only recently that the same generalized Planck law found for direct transitions is valid for indirect transitions as well [4]. According to this theory the rate of spontaneous emission dr_{em} of photons with energy between $\hbar\omega$ and $\hbar\omega + d\hbar\omega$ into the solid angle Ω is given by the absorption coefficient $\alpha(\hbar\omega)$ at exactly this photon energy and by the chemical potential μ_γ:

$$dr_{\mathrm{em}}(\hbar\omega) = \alpha(\hbar\omega)\frac{c_\gamma D_\gamma \Omega}{\exp[(\hbar\omega - \mu_\gamma)/kT] - 1}d(\hbar\omega), \tag{1}$$

$c_\gamma = c_0/n$ is the velocity of the photons in the emitting medium with refractive index n, and $D_\gamma = n^3(\hbar\omega)^2/4\pi^3\hbar^3c_0^3$ the density of states per solid angle for photons in the medium.

The chemical potential μ_γ of the emitted photons is equal to the difference, $\epsilon_{F,C} - \epsilon_{F,V}$, of the quasi-Fermi-energies, which describe separately the occupation of states in the conduction band and in the valence band. In thermal and chemical equilibrium with the surrounding blackbody radiation of 300 K, $\epsilon_{F,C} - \epsilon_{F,V} = \mu_\gamma = 0$ and Eq. (1) reduces to the original Planck law for thermal radiation. Although the dependence of the luminescence intensity on the absorption coefficient α in Eq. (1) is long known at least for direct transitions, no report could be found in the literature, in which values of the absorption coefficient had been obtained from luminescence.

As we will show in the following that photoluminescence is particularly useful to determine absorption coefficients at small photon energies. For a given luminescence quantum yield, which depends on the ratio of nonradiative to radiative lifetimes, a given number of photons has to be emitted. The denominator of Eq. (1) makes emission at large photon energies increasingly improbable and favors the emission at small photon energies, particularly at low temperatures, even if the absorption coefficient is small.

The emission rate given in Eq. (1) is not directly observable. It has to be integrated over the thickness of the sample to find the emitted photon current. For a planar slab with lateral extensions large compared to its thickness, which is homogeneously illuminated on the backside at $z = 0$, the energy current density dj_E emitted in the interval $d\hbar\omega$ from the front surface into a hemisphere is found by integrating Eq. (1) [5]:

$$dj_E(\hbar\omega) = M(\hbar\omega)\frac{c_0}{n^3}\pi D_\gamma(\hbar\omega)\alpha(\hbar\omega)\exp[-\alpha(\hbar\omega)d]\,d\hbar\omega \times \int_0^d \frac{\exp[\alpha(\hbar\omega)z] + R(\hbar\omega)\exp[-\alpha(\hbar\omega)z]}{\exp(\{\hbar\omega - [\epsilon_{F,C}(z) - \epsilon_{F,V}(z)]\}/kT) - 1}\,dz,$$

with

$$M(\hbar\omega) = \frac{1 - R(\hbar\omega)}{1 - [R(\hbar\omega)]^2\exp[-2\alpha(\hbar\omega)\,d]}. \tag{2}$$

This general emission formula accounts for multiple reflection by equal reflectivities $R(\hbar\omega)$ of both surfaces, for reabsorption of emitted photons and for inhomogeneities of the distribution of electrons and holes. For nondegenerate concentrations of electrons n_e and holes n_h, $\epsilon_{F,C}(z) - \epsilon_{F,V}(z) = kT\ln[n_e(z)n_h(z)/n_i^2]$, where n_i is the intrinsic concentration.

In general an exact knowledge of the spatial distribution of n_e and n_h and a quantitative measurement of the emission intensity $dj_E(\hbar\omega)$ is required to determine the absorption coefficient $\alpha(\hbar\omega)$ from luminescence via Eq. (2). In two cases the form of the emission spectrum in Eq. (2) does not depend on the charge carrier distribution and its dependence on the absorption coefficient becomes particularly simple, if the exitation conditions are well below the laser threshold, where $\hbar\omega - (\epsilon_{F,C} - \epsilon_{F,V}) \gg kT$.

(1) For homogeneous distributions of electrons and holes, which are present, if the diffusion lengths are much larger than the sample thickness d and if surface recombination is small

$$dj_E(\hbar\omega) \propto a(\hbar\omega)\,(\hbar\omega)^3\exp(-\hbar\omega/kT), \tag{3}$$

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where the absorptivity $a(\hbar\omega)$ is related to the absorption coefficient $\alpha(\hbar\omega)$ by

$$a(\hbar\omega) = [1 - R(\hbar\omega)]\frac{1 - \exp[-\alpha(\hbar\omega)\,d]}{1 - R(\hbar\omega)\exp[-\alpha(\hbar\omega)\,d]}\,. \quad (4)$$

(2) For weak absorption, $\alpha(\hbar\omega)d \ll 1$, the form of the emission spectrum does not depend on the distribution of electrons and holes, since reabsorption is negligible:

$$dj_E(\hbar\omega) \propto \alpha(\hbar\omega)d(\hbar\omega)^3\exp(-\hbar\omega/kT). \quad (5)$$

In these special cases a quantitative measurement of the luminescence intensity is not necessary to find the spectral dependence of the absorption coefficient α. For the homogeneous distribution of the charge carriers in case (1), only one value of the absorptivity must be known, e.g., the saturation value, $a(\hbar\omega) = 1 - R(\hbar\omega)$, at photon energies, where $\alpha d \gg 1$. The absorption coefficient then follows from Eqs. (3) and (4). Alternatively, as in the case of weak absorption, one value of the absorption coefficient must be known from the literature at a photon energy within the emission spectrum, from which the constant of proportionality in either Eq. (3) or (5) is fixed.

The above considerations have been applied to our experimental investigations of the photoluminescence of silicon. The samples were illuminated from the rear by a laser diode emitting at 790 nm. The penetration depth at the laser wavelength is 11 μm. The luminescence was measured from the front side. With its thickness of more than 250 μm, the sample itself very effectively blocks the laser light from reaching the detector. Low intensity emission of the laser diode at longer wavelengths, which would be transmitted by the sample, was blocked by an interference filter centered on the laser wavelength. The photoluminescence radiation was passed through a 1/4 m monochromator with a grating blazed at 1000 nm and was detected by a liquid-N_2-cooled Ge P-I-N diode. Great care was taken that neither transmitted nor scattered laser radiation reached the detector. The transmittance of the monochromator was calibrated with a known blackbody spectrum from a tungsten halogen lamp, the Ge diode was calibrated against a black pyroelectric detector. The intensity of the laser diode was modulated sinusoidally at 565 Hz and the detector signal was measured with a current-voltage converter and a lock-in amplifier. The overall wavelength resolution was 7 nm.

Two Si samples of p-type boron doped float zone material were investigated. Sample A had a resistivity of 0.5 Ω cm and a thickness of $d = 262$ μm, sample B had 16 Ω cm and $d = 535$ μm. Both surfaces of the samples were polished and well passivated by a thermally grown oxide of 100 nm thickness, which allows us to neglect surface recombination. Since the diffusion length of the minority carriers was also much larger than the thickness of the samples, a variation of their concentration perpendicular to the surface could be neglected. The reflectivity of the samples was measured directly and was taken into account in determining the absorption coefficient.

Luminescence at 90 K—Photoluminescence spectra of both samples are shown for 90 K in Fig. 1. The luminescence is observed at photon energies, at which both samples are weakly absorbing ($\alpha d \ll 1$) and Eq. (5) is applicable. For both samples the luminescence intensity is normalized to 1 at the maximum of the spectra, which removes the influence of the different thicknesses. The differences in the spectra on the low energy side can be attributed to transitions from the conduction band into empty boron acceptor levels. At 90 K about 60% of the acceptor states are not occupied by electrons in the 0.5 Ω cm material of sample A and 98% in the 16 Ω cm material of sample B. The enhanced luminescence at 1.07, 1.01, and 0.95 eV is due to transitions designated by B_3^{TO}, B_5^{TO}, and $B_5^{\mathrm{TO}} + O^{\Gamma}$ in [6]. The peak at 0.915 eV could not be identified.

Most emitted photons have energies below the band gap of silicon of $\epsilon_G = 1.167$ eV at 90 K [7]. Photon emission then occurs in combination with phonon emission. In a transmission experiment photon absorption at these photon energies requires phonon absorption. Because of the low density of phonons at 90 K photon absorption is rather improbable and is unmeasurably small, only on the high energy side of the luminescence spectrum, where in a transmission experiment photon absorption is accompanied by phonon emission, can photon absorption be detected and data for the absorption coefficient are available. Using the value of the absorption coefficient of $\alpha = 0.061$ cm^{-1} at 1.164 eV from the data by MacFarlane *et al.* [8], values for the absorption coefficient at other photon energies were calculated from the luminescence spectra with Eq. (5) and are shown in Fig. 2 together with the data by McFarlane *et al.* With our new method of obtaining the absorption coefficient from lumi-

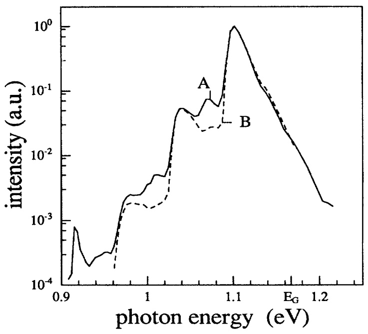

FIG. 1. Photoluminescence intensity as a function of the photon energy at 90 K for two silicon samples, sample A has 0.5 Ω cm resistivity and 262 μm thickness (solid line) and sample B has 16 Ω cm resistivity and 535 μm thickness (broken line). Both samples have polished and oxide-passivated surfaces.

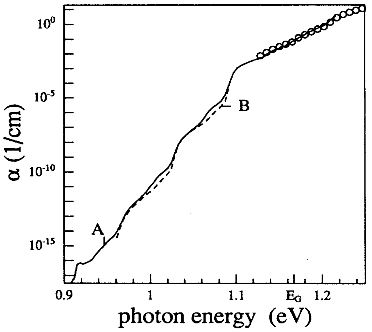

FIG. 2. Absorption coefficient of silicon at 90 K as a function of the photon energy obtained from the luminescence spectra in Fig. 1 in comparison with the data obtained from transmission by MacFarlane *et al.* [8] (circles).

nescence the absorption spectrum of silicon is extended to well below the band gap with values as small as 10^{-16} cm^{-1}, which are impossible to observe in transmission, while good agreement is found in the photon energy range for which transmission data exist.

Luminescence at 295 K—Figure 3 shows the luminescence spectra for the two samples at 295 K. Using Eq. (3), the absorptivity is determined in arbitrary units and is also shown in Fig. 3 for sample A. According to Eq. (4) the two spectra must differ at low photon energies, where $\alpha d \ll 1$ by the factor $f = (1 - R_B)d_B/(1 - R_A)d_A$. The luminescence intensity was therefore normalized at the maximum of the spectrum to 1 for sample A and to f for sample B. On the high energy side of the spectrum, where the absorptivity is saturated, the spectrum is independent of the absorption coefficient α and independent of the thickness, hence $\alpha d \gg 1$ and the absorptivity must have the value $a = 1 - R$. Transitions from the conduction band to empty acceptor states are no longer observed, since at 295 K the acceptor states are fully occupied in both samples.

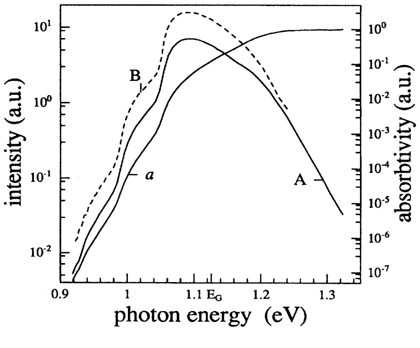

FIG. 3. Photoluminescence intensity as a function of the photon energy at 295 K of the silicon samples described in Fig. 1. The absorptivity $a(\hbar\omega)$ of sample A is shown in arbitrary units as it follows from Eq. (3). At larger photon energies, where the absorptivity saturates, it is $a(\hbar\omega) = 1 - R(\hbar\omega)$.

Knowing that $a = 1 - R$ on the high energy side of the luminescence spectrum, values for the absorptivity at smaller photon energies are obtained from the luminescence spectrum with Eq. (3). The absorption coefficient is then found from Eq. (4) and is shown in Fig. 4 together with data by MacFarlane *et al.* [8]. Again, good agreement is found with the data obtained from transmission.

In conclusion, we have presented a method to extract values of the absorption coefficient of silicon from its luminescence spectrum by relying on the predictions of the generalized Planck emission law. It turns out that this is a particularly useful method for small absorption coefficients and values as small as 10^{-16} cm^{-1} have been found. This procedure is valid for transitions between states, which are occupied according to the quasi-Fermi-distribution either for the conduction band or for the valence band. This includes transitions between the conduction band and shallow acceptor states as was observed in the spectra at 90 K. It also includes transitions between shallow donors and the valence band or between shallow donors and shallow acceptors, which were not observed in our p-type samples. In a general case, finding quantitative values of the absorption coefficient requires the knowledge of the spatial distribution of the concentrations of electrons and holes and quantitative measurements of the luminescence intensity. In two special cases, where either the absorptivity is small ($\alpha d \ll 1$) or the carrier concentrations are homogeneous, a procedure is described by which values of the absorption coefficient are calculated from the luminescence spectrum by a fit to one value known from a transmission experiment. If, however, the luminescence spectrum extends to photon energies where the absorptivity is saturated ($\alpha d \gg 1$), as it occurs in silicon at or above room temperature, we have shown that no foreign data are necessary to obtain quantitative values of the absorption coefficient. This method was demonstrated for indirect transitions in silicon, but it is applicable to other materials and to direct transitions as well.

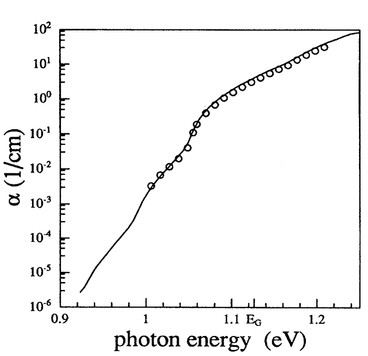

FIG. 4. Absorption coefficient of silicon at 295 K as a function of the photon energy obtained from the absorptivity a in Fig. 3 in comparison with the data obtained from transmission by MacFarlane *et al.* [8] (circles).

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