

HEAVILY DOPED SILICON STUDIED BY LUMINESCENCE AND SELECTIVE ABSORPTION

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Abstract—Low temperature photoluminescence and selective absorption (photoluminescence excitation spectroscopy) measurements are used to study heavily doped *n*- and *p*-type silicon. From the selective absorption spectra, an accurate determination of the optical band gap up to charge carrier concentrations of $1.5 \times 10^{19} \text{ cm}^{-3}$ was performed. For carrier concentrations in the range of 10^{17} – 10^{18} cm^{-3} impurity-induced no-phonon band-to-band absorption was observed in addition to the normal phonon assisted indirect interband absorption. In the emission spectra an increase of the no-phonon and of the TA-phonon assisted recombination, compared to the TO-phonon assisted emission, was found for carrier concentrations above $2 \times 10^{19} \text{ cm}^{-3}$. This indicates an impurity induced change in the transition matrix elements.

1. INTRODUCTION

Heavy doping of silicon causes a reduction of the fundamental band gap and, for degenerate material, a filling of the conduction or valence band[1]. In addition, band tailing effects occur due to the random distribution of the impurities. Values for the band gap reduction have been derived from electrical transport experiments[2] as well as from optical measurements like absorption[3–5], photoluminescence (PL)[6–9] and photoluminescence excitation (PLE) spectroscopy[9].

PL experiments measure the carrier distribution within the conduction or valence band (for *n*- or *p*-type doping, respectively) as well as the band gap energy via the radiative recombination of minority carriers[7, 9]. The luminescence band extends from the reduced band gap energy $E_{G,2}$ (low energy edge) to the energy of the optical gap $E_{G,1}$ (high energy cutoff). The width of the emission band represents the band filling E_F (see Fig. 1), which is the difference between $E_{G,1}$ and $E_{G,2}$. Due to the indirect band structure of silicon this luminescence band occurs in different phonon replicas, involving momentum conserving transverse acoustic (TA) and transverse optic (TO) phonons.

In conventional absorption experiments, where the intensity of the light transmitted through the sample is recorded, two types of absorption processes are measured simultaneously. One process is the absorption of an electron out of the valence band into the conduction band. The minimum photon energy required for this band-to-band process is $E_{G,1}$. The other absorption mechanism is the excitation of an electron (hole) within the conduction (valence band), the so-called free carrier absorption. In the absorption spectrum of heavily doped silicon both absorption processes are strongly overlapping[5]. Therefore

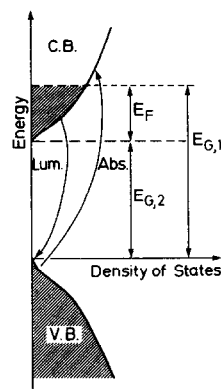


Fig. 1. Schematic drawing of the density of states of a heavily doped *n*-type semiconductor. Optical band gap $E_{G,1}$ and reduced band gap $E_{G,2}$ as well as the band filling E_F are indicated.

it is necessary to deconvolute the spectra by fitting the low energy part of the spectrum with a model for the free carrier absorption and to subtract that fitted curve from the measured spectrum to obtain the band-to-band absorption[5].

PLE spectroscopy monitors the intensity of the luminescence transition discussed above as a function of the excitation photon energy. In order to observe this luminescence the absorbed light has to create minority carriers. Therefore the PLE—or selective absorption—technique is only sensitive to band-to-band excitations[9], in contrast to conventional absorption measurements.

Taking advantage of this fact, the shift of the optical band gap in silicon was studied in the doping range from 10^{17} to 10^{19} carriers/ cm^3 . For carrier concentration in the range from 10^{17} to 10^{18} cm^{-3} impurity-induced no-phonon band-to-band absorption was detected. A detailed lineshape analysis of the emission (PL) spectra revealed a significant increase in relative intensity of both the no-phonon

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and the transverse acoustic (TA) phonon assisted luminescence for carrier concentration exceeding $2 \times 10^{19} \text{ cm}^{-3}$. The relative strength of the phonon assisted and no-phonon optical transitions is again an important parameter in the analysis of conventional absorption spectra[4, 5].

2. EXPERIMENTAL

The samples were bulk doped with phosphorus or boron. The charge carrier concentration was determined from room temperature conductivity and checked by the measurement of the plasma frequency, which was obtained from the minimum in ir reflectivity[10].

The samples were cooled to 5 K by He exchange gas. For the PL experiments the luminescence was excited by the 647 nm line of a Kr^+ laser. For the excitation spectroscopy (PLE) a tunable color center laser was used. With NaF crystals containing $(\text{F}_2^+)^*$ centers[11,12] a tuning range from 1.01 to 1.13 μm was obtained and using LiF:F_2^+ crystals[13] the spectral range from 0.975 to 1.04 μm was covered. The luminescence was analyzed with a 1 m double monochromator and detected with an intrinsic Ge photodiode cooled to liquid nitrogen temperature.

3. RESULTS AND DISCUSSION

A. Selective absorption

PLE spectra for samples doped with phosphorus or boron in concentrations just below the critical value of $3 \times 10^{18} \text{ cm}^{-3}$ [14] for the insulator-metal transition are displayed in Fig. 2. Also shown is the excitation spectrum of the free exciton luminescence in a pure sample. Comparing this spectrum with conventional absorption spectra[15] the step at 1056 nm is identified with the onset of TA-phonon-

assisted and the step at 1022 nm with the onset of TO-phonon-assisted free-exciton absorption.

For Si:B ($2 \times 10^{18} \text{ cm}^{-3}$) two humps appear at 1060 (TA replica) and 1026 nm (TO replica) in the excitation spectrum[16], which are associated with the transition of an electron out of a filled state in the acceptor impurity band into the conduction band[9]. The minima in the emission intensity at the short wavelength side of the impurity band related absorption (IB(TA), IB(TO)) are used to define the onset of band-to-band absorption ($E_{G,1}(\text{TA})$, $E_{G,1}(\text{TO})$). In contrast to the PLE spectrum of the pure sample, where only phonon assisted absorption processes occur, in the spectrum of the boron doped sample a structure appears at 1078 nm, which is the no-phonon replica of the impurity band related transitions (IB^{NP}). At the high energy side of the IB^{NP} peak also the onset of no-phonon band-to-band absorption is observed. In the phosphorus doped sample ($8 \times 10^{17} \text{ cm}^{-3}$) a similar excitation spectrum is obtained with well-resolved structures in the TO- and no-phonon replica. The IB^{NP} peak is more intense, compared to the no-phonon band-to-band absorption, as for the boron doped sample.

For excitons bound to isolated donors or acceptors, no-phonon recombination as well as absorption is known[17]. Also for heavily doped material zero phonon emission is reported in the literature[6, 9]. In contrast unambiguous no-phonon band-to-band absorption, which involves conduction and valence band states rather than bound exciton states, is observed for the first time in heavily doped silicon. The no-phonon recombination is relatively strong for P and As and very weak for B[6, 9, 17]. The same applies, to some extent, to the impurity band no-phonon absorption. The no-phonon band-to-band transitions, however, are, within the experimental accuracy, of equal strength for P and B doped material.

The contribution of no-phonon transitions to the band-to-band absorption in heavily doped Si has been discussed, based on conventional absorption experiments, in the literature[3–5]. According to Balkanski *et al.*[4], no-phonon absorption is dominant in heavily phosphorus doped silicon. The results obtained by Vol'fson and Subashiev[3] and by Schmid[5], however, show no indication of phononless absorption processes. The present work shows that the no-phonon contribution to band-to-band absorption is too weak, at least for carrier concentrations around 10^{18} cm^{-3} , to be observed for photon energies above $E_{G,1}(\text{TO})$ as used in conventional absorption. The strength of the no-phonon absorption amounts only to about 1/3 of that of the TA-phonon assisted transitions, which are in turn about one order of magnitude weaker than the TO phonon assisted absorption[15] (see Fig. 2).

Figure 3 displays the square root of the luminescence intensity plotted versus exciting laser wavelength for phosphorus and boron doped samples with carrier concentrations above the insulator-metal

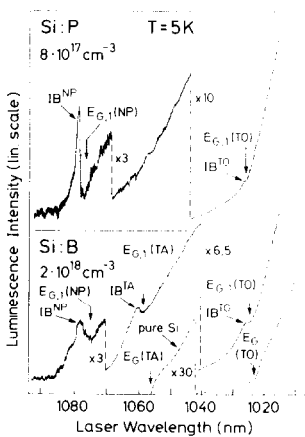


Fig. 2. PLE spectra of Si:P and Si:B. The lowest dashed curve shows for comparison an excitation spectrum of the free exciton luminescence in a pure sample. IB indicates impurity band related absorption, E_G (pure sample) and $E_{G,1}$ (doped samples) mark the onset of band-to-band absorption. TO, TA, and NP refer to TO-phonon, TA phonon assisted and no-phonon transitions, respectively.

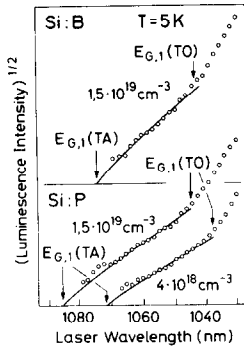


Fig. 3. Square root of the luminescence intensity plotted versus exciting photon wavelength for Si:P (4×10^{18} and 1.5×10^{19} carriers/cm³) and Si:B (1.5×10^{19} carriers/cm³). $E_{G,1}(TO)$ and $E_{G,1}(TA)$ denote the onset of TO- and TA-phonon assisted band-to-band absorption. The drawn lines are fitted absorption curves (see text).

transition. The PLE spectra show a constant increase in luminescence with increasing exciting photon energy and no structures are observed any more[9]. The low energy part of the spectra is due to TA-phonon assisted absorption. The increase in slope at higher photon energies indicates the onset of absorption transitions with TO-phonon participation. It can be shown that the luminescence intensity recorded in the PLE experiment is proportional to the band-to-band absorption coefficient, if this coefficient is small compared to the inverse thickness of the sample or to the total absorption coefficient (i.e. the sum of the coefficients for band-to-band and intraband absorption). Under these conditions, which are fulfilled in the present experiments, the measured PLE spectra can be compared directly to calculated absorption curves.

For indirect band-to-band absorption in a pure semiconductor at low temperature the absorption coefficient α_0 can be written as[4]

$$\alpha_0 \sim (\hbar\omega - E_G - \hbar\omega_{ph})^2, \quad (1)$$

where $\hbar\omega$ is the energy of the absorbed photon, E_G is the band gap energy and $\hbar\omega_{ph}$ is the energy of the emitted momentum conserving phonon. In heavily doped samples the absorption edge is modified due to the bandfilling. The absorption coefficient is then given by[5,18]

$$\alpha \sim \alpha_0 \int_0^1 \frac{x^{1/2}(1-x)^{1/2} dx}{1 + \exp\left(\frac{E_F - x(\hbar\omega - E_G - \hbar\omega_{ph})}{kT}\right)}. \quad (2)$$

At low temperature the absorption edge is shifted to higher energies by E_F (see Fig. 1) and the slope of the absorption curve becomes steeper than for pure material[5,18].

The part of the PLE spectra showing TA phonon assisted transitions was fitted with an absorption curve calculated using eqns (1) and (2) to determine

the position of the TA phonon absorption edge $E_{G,1}(TA)$. As it can be seen from Fig. 3 a good fit is obtained assuming only TA-phonon assisted absorption. This indicates that also for samples with $\approx 10^{19}$ carriers/cm³ the no-phonon absorption is weaker than the TA phonon transitions and cannot be resolved within the noise limits. The TO phonon absorption edge was obtained from the change in the slope of the PLE spectra at 1.04–1.05 μ m.

The optical band gap determined by excitation spectroscopy is shown in Fig. 4 as a function of the carrier concentration together with data obtained from PL experiments[9]. All the data displayed have been corrected for the energies of the momentum conserving phonons involved. For carrier concentrations below the metal-insulator transition ($\approx 3 \times 10^{18}$ cm⁻³) the position of the band-to-band absorption edge remains rather constant. This indicates that in the present doping range the shrinkage of the band gap is compensated by the reduction of the free exciton binding energy due to screening effects. (For a carrier concentration of $\approx 3 \times 10^{18}$ cm⁻³ the exciton binding energy is expected to become zero.) The position of the high energy cutoff of the impurity band (IB) luminescence is also independent of the carrier concentration. The difference in energy between the PL and PLE data gives the separation between the filled (empty) states of the donor (acceptor) impurity band and the bottom (top) of the conduction (valence) band. For carrier concentrations exceeding the critical value of 3×10^{18} cm⁻³ a slight reduction of the optical gap occurs. This reduction is somewhat larger for *n*- than for *p*-type material. The gap energies determined by PL and PLE are in good agreement within the experimental error. In most of the samples, however, the energy values obtained from the high energy edge of the PL spectra are slightly larger than the ones deduced from PLE data. This might be due to additional

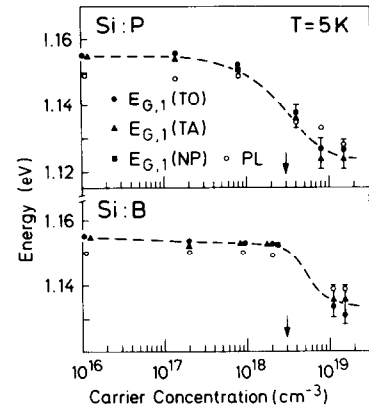


Fig. 4. Positions of the optical band gap $E_{G,1}$ as determined from the onset of no-phonon, TA- and TO-phonon assisted band-to-band absorption. Also shown is the high energy cutoff of the photoluminescence. All data have been corrected for the phonon energies involved. Critical Mott density is indicated by an arrow.

heating of the samples in the PL measurements compared to the PLE experiment caused by the excess laser photon energy and the small penetration depth of the exciting light[9]. As it can be seen from eqn (3) (see Section 3B), the high energy edge of the emission reflects the thermal distribution of the carriers. Therefore at a constant band filling an increase in carrier temperature shifts the high energy edge to larger energies.

B. Emission line shape

For indirect band-to-band transitions, where momentum conservation is fulfilled by phonon participation or by impurity scattering, the emission line shape $I(h\nu)$ can be expressed 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) assuming constant transition matrix elements[19]:

$$I(h\nu) \sim \int_0^\infty f_e(E) D_e(E) f_h(h\nu - E_{G,2} - E) \times D_h(h\nu - E_{G,2} - E) dE. \quad (3)$$

For n -type (p -type) material $f_e(E)$ ($f_h(E)$) is the Fermi distribution function and, assuming thermalization of the minority carriers, $f_h(E)$ ($f_e(E)$) can be described by a Boltzmann distribution. To account for band-tailing effects, incomplete thermalization of the carriers and the finite resolution in the experiment, a Gaussian broadening of $I(h\nu)$ is introduced[7]

$$\bar{I}(h\nu) = \int_0^\infty I(h\nu') \cdot e^{-(h\nu' - h\nu/E_s)^2} dh\nu' \quad (4)$$

with E_s as a broadening parameter.

Figure 5 displays typical PL spectra for n - and p -type silicon[9]. Also shown is the emission line shape calculated using eqns (3) and (4). To account for the overlapping TA, TO and TO + O^Γ phonon replicas (O^Γ denotes the zone-centre optical phonon), and, for n -type material, for the no-phonon replica in the experimental spectra three (p -type) or four (n -type) curves were superimposed, with a relative displacement equal to the energy of the phonon participating in that particular transition. The fitting parameters were the band filling E_F , the broadening E_s and the relative intensities of the phonon replicas. The temperature of the charge carriers found in all the spectra analyzed was 20 K. This is somewhat higher than the temperature of the exchange gas (5 K), due to the heating of the sample by the exciting laser light (power density 200–400 W/cm²)[9]. For n -type material a parabolic conduction band was assumed, whereas for p -type samples the complex structure of the valence band was taken into account, which leads to nonparabolicities in the density of states[20].

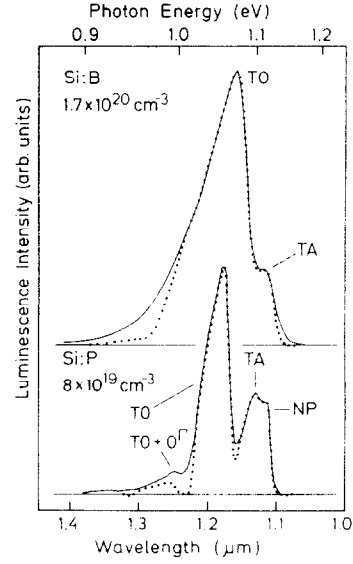


Fig. 5. PL spectra (drawn line) for Si:P (8×10^{19} carriers/cm³) and Si:B (1.7×10^{20} carriers/cm³). The dotted curves show calculated emission line shapes fitted to the experimental spectra. Fitting parameters are given in the text.

The overall agreement between experimental and fitted line shape is good for the whole series of spectra analyzed ranging from carrier concentrations of 4×10^{18} cm⁻³ up to 4×10^{20} cm⁻³ (see Fig. 5). On the low energy side, however, the calculated line shape shows a steeper decrease in luminescence intensity as observed in the experiment. This might be due to the rather simple way used in eqn (4) to account for band tailing effects, which seems to underestimate the density of states in the band tails. The minor discrepancy at the high energy edge of the PL spectrum of Si:B 1.7×10^{20} cm⁻³ is due to a small no-phonon contribution to the recombination which has been neglected in the line shape calculation.

The band filling E_F obtained from the line shape analysis is plotted in Fig. 6 vs the carrier concentra-

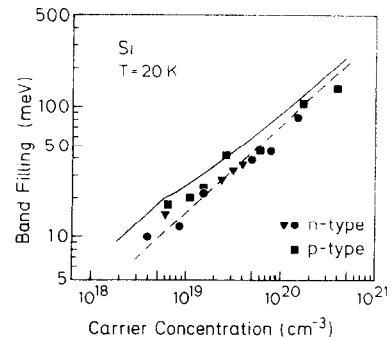


Fig. 6. Band filling for n -type ($\bullet$ Si:P, this work; $\blacktriangledown$ Si:As, Ref. 7) and p -type ($\blacksquare$ Si:B, this work) material as obtained from line shape analysis. Calculated band filling for n -type (dashed line) and p -type (drawn line) doping is also shown.

tion. The broadening parameter E_S used for the fitting procedure was 10–20% of E_F . Also included are the experimental data for n -type material reported by Dumke[7]. For comparison the calculated dependence of E_F on the carrier concentration is also shown. For n -type doping a constant density of states mass of $1.062 m_0$ was assumed for the conduction band[21], whereas for p -type samples the density dependent valence band density of states mass given by Barber[20] was used. The band filling for p -type material found experimentally is larger than the filling for n -type doping as is expected from the difference in the density of states masses of conduction and valence band[9]. The band filling obtained from the line shape analysis is somewhat smaller (compared to the calculated data) for both n - and p -type doping. This is again a consequence of the rather simple way used here to account for the band tailing. The discrepancy between calculated and experimentally observed band filling for the most heavily doped p -type samples possibly indicates a systematic deviation of the hole density of states mass from the values calculated by Barber using the valence band parameters of lightly doped silicon[22].

Another point of interest is the variation of the relative phonon replica intensities upon doping. Figure 7 displays the intensity of no-phonon (for n -type doping) and of the TA-phonon replica, measured relative to the TO-phonon replica, as obtained from the line shape analysis. The relative intensity of the TA as well as of the no-phonon band increases for carrier concentrations exceeding $\approx 2 \times 10^{19} \text{ cm}^{-3}$. From the present experiments it cannot be seen whether the TO-phonon replica decreases or, for example, the no-phonon band increases in absolute intensity. But keeping in mind the PLE results from Section 3.A showing no-phonon band-to-band absorption in contrast to lightly doped samples, it is reasonable to assume an increase of phononless radiative transitions rather than a decrease in TO-phonon coupling. The no-phonon intensity increases

for Si:P by a factor of 2.5 when increasing the dopant concentration from $\approx 10^{19} \text{ cm}^{-3}$ to $1.5 \times 10^{20} \text{ cm}^{-3}$, indicating a significant increase of large wavevector impurity scattering.

The observed increase in relative intensity of the TA phonon band is rather surprising because the TA-phonon assisted recombination in silicon is allowed by symmetry[23]. In the experiment, however, the TA-phonon participation resembles more a partially forbidden transition, which gains increasing strength when the selection rules are relaxing upon doping. The present experimental finding is consistent with experimental results obtained by Voisin *et al.*[24]. These authors investigated the TA- and TO-phonon assisted radiative recombinations of free excitons and electron-hole drops in pure silicon and found that for the TA replica the electron-phonon matrix element should be taken as k -dependent. This again gives the TA-phonon assisted recombination the character of a partially forbidden process.

A possible explanation for these experimental findings can be obtained from following considerations. Indirect optical transitions from the Δ -line along the [100] direction in the band structure (symmetry Δ_1) to the top of the valence band at the Γ point (symmetry Γ'_{25}) are allowed for TA phonon assisted transitions with both the Γ_{15} conduction band and the Δ_5 valence band as intermediate states[23]. Considering the optical transition from the X point in the conduction band (symmetry X_1) to the Γ'_{25} valence band, however, only the transition via the Γ_{15} conduction band intermediate state is symmetry allowed with TA-phonon participation. With the minimum in the conduction band in the [100] direction at about 85% of the way to the zone boundary (X point)[23], it is reasonable to consider the TA-phonon assisted transitions as a partially forbidden process, which therefore gains strengths with increasing impurity concentration.

4. CONCLUSIONS

Using PLE spectroscopy a detailed study of the band-to-band absorption edge has been performed in heavily doped n - and p -type silicon. For charge carrier concentrations around 10^{18} cm^{-3} no-phonon band-to-band transitions are found in addition to the phonon-assisted absorption known from pure and lightly doped silicon. For carrier concentrations above the critical Mott density the optical band gap position determined from PLE and luminescence are in good agreement. A detailed line shape analysis of the emission spectra revealed an increase in strength of the TA-phonon assisted and no-phonon recombination band relative to the TO-phonon replica for dopant concentrations exceeding $\approx 2 \times 10^{19} \text{ cm}^{-3}$. The dopant density dependence of the no-phonon line indicates an increase of large wavevector impurity scattering for high doping levels. The change in relative strength of the TA replica can be understood

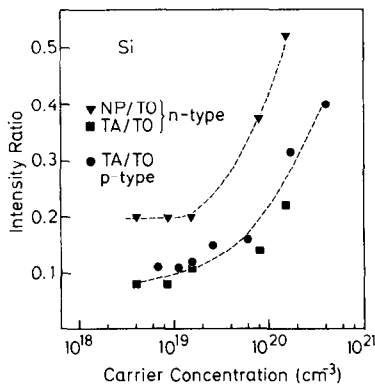


Fig. 7. Relative intensities of no-phonon and TA-phonon replica versus charge carrier concentration for n -type (Si:P) and p -type (Si:B) material. The dashed curves are drawn as a visual guide.

when considering the TA phonon assisted optical transition as a partially forbidden one.

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REFERENCES

1. R. A. Abram, G. J. Rees and B. L. H. Wilson, *Adv. Phys.* **27**, 799 (1978).
2. J. W. Slotboom and H. C. de Graaf, *Solid-St. Electron.* **19**, 857 (1976).
3. A. A. Vol'fson and V. K. Subashiev, *Fiz. Tekh. Poluprovodn.* **1**, 397 (1967) *Sov. Phys.-Semicond.* **1**, 327 (1967).
4. M. Balkanski, A. Aziza and E. Amzallag, *Phys. Status Solidi* **31**, 323 (1969).
5. P. E. Schmid, *Phys. Rev.* **B23**, 5531 (1981).
6. P. E. Schmid, M. L. W. Thewalt and W. P. Dumke, *Solid State Commun.* **38**, 1091 (1981).
7. W. P. Dumke, *Appl. Phys. Lett.* **42**, 196 (1983).
8. W. P. Dumke, *J. Appl. Phys.* **54**, 3200 (1983).
9. J. Wagner, *Phys. Rev.* **B29**, 2002 (1984).
10. V. I. Fistul, *Heavily Doped Semiconductors*, Plenum, New York (1969).
11. L. F. Mollenauer, *Opt. Lett.* **5**, 188 (1980).
12. J. Wagner, J. Weber and R. Sauer, *Solid State Commun.* **39**, 1273 (1981).
13. L. F. Mollenauer, D. M. Bloom and A. M. DelGaudio, *Opt. Lett.* **3**, 48 (1978).
14. N. F. Mott, *Proc. Phys. Soc. (London)* **62**, 416 (1949); T. G. Castner, N. K. Lee, G. S. Cieloszyk and G. L. Salinger, *Phys. Rev. Lett.* **34**, 1627 (1975); R. R. Parsons, J. A. Rostworowski and B. Bergersen, in *Proceedings of the 14th International Conference on the Physics of Semiconductors, Edinburgh, 1978*, (edited by B. L. H. Wilson), Institute of Physics, London (1979), p. 1267.
15. G. G. MacFarlane, T. P. McLean, J. E. Quarrington and V. Roberts, *Phys. Rev.* **111**, 1245 (1958).
16. For recording the PLE spectra the luminescence from the recombination of majority carriers with minority carriers trapped to compensating impurities (so-called low-level emission) was used as the monitor, because this recombination was the strongest under resonant excitation (see [9]).
17. P. J. Dean, J. R. Haynes and W. F. Flood, *Phys. Rev.* **161**, 711 (1967).
18. J. I. Pankove and P. Aigrain, *Phys. Rev.* **126**, 956 (1962).
19. R. R. Parsons, *Solid State Commun.* **29**, 763 (1979).
20. H. D. Barber, *Solid-St. Electron.* **10**, 1039 (1967).
21. G. Dresselhaus, A. F. Kip and C. Kittel, *Phys. Rev.* **98**, 368 (1955).
22. J. C. Hensel and G. Feher, *Phys. Rev.* **129**, 1041 (1963).
23. M. Lax and J. J. Hopfield, *Phys. Rev.* **124**, 115 (1961).
24. P. Voisin, M. Voos and C. Benoit à la Guillaume, *Solid State Commun.* **31**, 901 (1979).