Electron-hole liquid in GaP:N

J. E. Kardontchik and E. Cohen
Department of Physics and Solid State Institute, Technion—Israel Institute of Technology, Haifa, Israel
(Received 19 January 1978; revised manuscript received 10 April 1978)

The radiative recombination of the nitrogen-induced electron-hole liquid in GaP:N is observed. The liquid is formed by delocalization of excitons bound to nitrogen in crystals in which the nitrogen concentration exceeds 10^{17} cm^{-3}, and under intense band-gap or selective excitation into the lowest $J = 1$ state of the bound exciton (A line). The observed binding energy is 17 meV relative to the free-exciton level. The liquid density is in the range of $(1–4) \times 10^{18}$ cm^{-3} for excitation intensity varying in the range of 10^{14}–10^{18} photons/cm^2/pulse.

I. INTRODUCTION

Recently the electron-hole liquid (EHL) has been observed in GaP[1-3] as well as in other polar semiconductors. Relatively pure GaP crystals have been used in these studies, and the EHL is observed through its phonon-assisted radiative recombination. It is well known[4] that nitrogen dopants in GaP form isoelectronic traps. At low temperatures, bound excitons recombine radiatively at the N trap (or at nitrogen pair traps if $[N] \geq 10^{18}$ cm^{-3}) with quantum efficiency of approximately unity.[5] Schwabe *et al.*[6] have reported the observation of a new radiative recombination band in crystals doped with $[N] > 10^{18}$ cm^{-3} and excited with a N_2 laser, which they attributed to the no-phonon transition of the EHL due to breaking of the $\underline{k}$ selection rule at the isoelectronic traps.

In this paper we present experimental results indicating that the role of the nitrogen impurities inducing the new high-intensity band is quite different. In contradistinction to the known cases (pure and doped Ge and Si, pure polar semiconductors) in which the EHL is formed by condensation of free excitons, in heavily doped GaP:N the EHL is formed of a high density of delocalized excitons which are provided by the nitrogen impurities. There are two requirements for the formation of this EHL. The first is that the concentration of nitrogen be sufficiently large that the interimpurity distance be of the same order of magnitude as that of the exciton Bohr radius ($a_0 = 40$ Å)[7] so that exciton delocalization takes place.[8] The second requirement is that all the nitrogen traps be populated in a time short compared with the exciton lifetime. (At low temperatures it is the radiative lifetime of the A line, $\tau_A = 40$ nsec.[9]) In this way a high density of bound excitons is obtained and these can migrate in the nitrogen system. This unique role played by the nitrogen impurities is demonstrated by observing the EHL radiative recombination under selective excitation into the lowest $J = 1$ state of the exciton bound to nitrogen.

The paper is outlined as follows: Sec. II presents the experimental procedure and results. Section III details the analysis and Sec. IV is a short summary.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Several crystals doped with nitrogen concentration varying from 10^{15} to 10^{19} cm^{-3} were studied.[10] They were excited with a tunable pulsed dye laser pumped with a N_2 laser. Front surface excitation was used in all experiments. The laser pulse width was 5 nsec, its peak power 10 kW, linewidth of 0.2 meV and the repetition rate used was 15 Hz. The excitation photon energies used were 2.65, 2.37 (near the indirect band gap), and 2.317 eV, which is the energy of the A line of the exciton bound to N. The background fluorescence of the dye laser was removed by an additional extracavity grating. The luminescence was detected with a double monochromator equipped with a fast photomultiplier. The signals were processed with a boxcar averager with a gate of 1 nsec, unless otherwise stated. The overall time resolution of the system was 5 nsec (limited by the photomultiplier response time). The crystals were immersed either in liquid helium or in a controlled stream of helium gas for temperatures higher than 4.2 K.

Figure 1 compares the luminescence spectra obtained from several GaP:N crystals excited with 2.65-eV radiation and a photon flux of 10^{18} cm^{-2} per pulse. (Henceforth we shall use photons/cm^2 per pulse as units of excitation intensity.) The nominally undoped crystal (actually containing 10^{15} N/cm^3 and some donors) shows the phonon-assisted radiative recombination of the EHL, similar to that reported in Refs. 1–3. For nitrogen concentrations of 10^{16}–10^{17} cm^{-3} the EHL is not observed and the spectrum is similar to that obtained under low-level cw excitation [cf. Figs. 1(c) and 2(c)]. For $[N] = 2 \times 10^{17}$ cm^{-3} [Fig. 1(b)] the spectrum consists

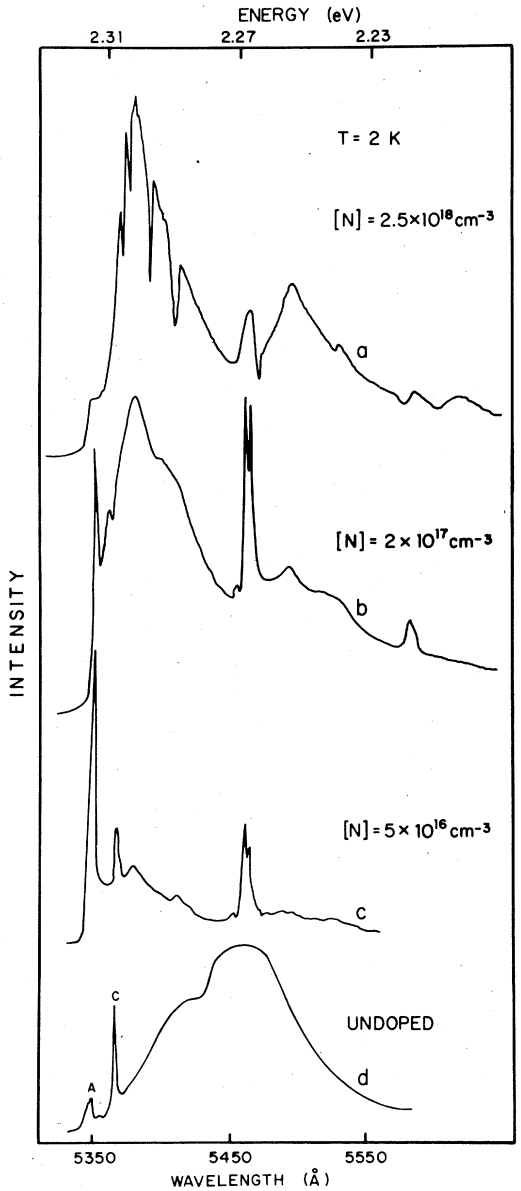

FIG. 1. Luminescence spectra of GaP crystals doped with various nitrogen concentrations. A pulsed dye laser was used for excitation with photon energy of 2.65 eV and intensity of 10^{18} photons/cm^2 per pulse.

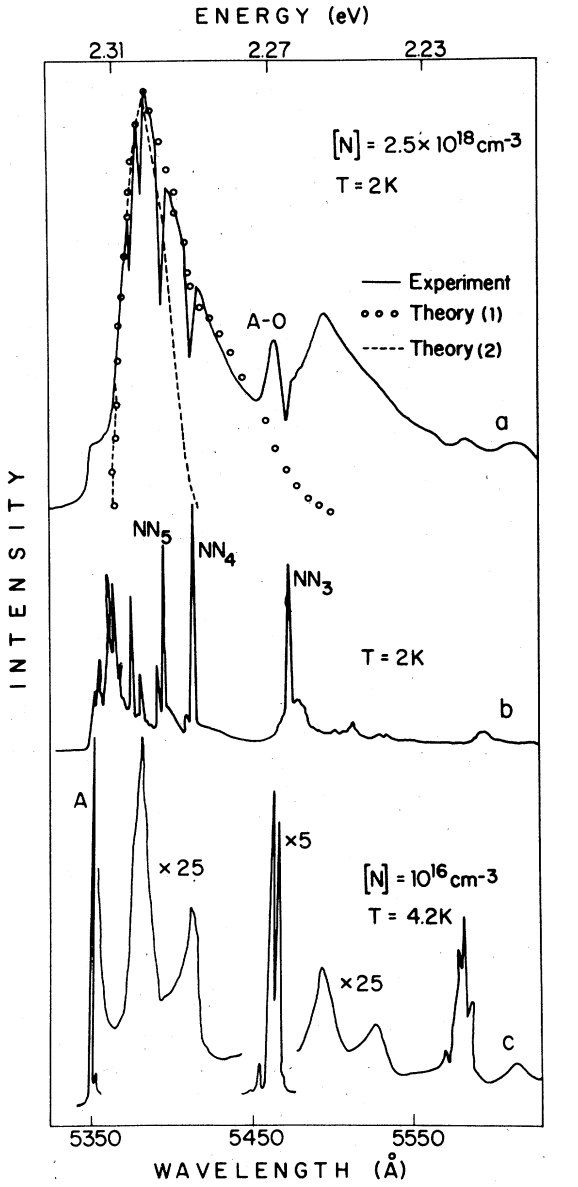

FIG. 2. (a) Electron-hole liquid radiative recombination in GaP doped with 2.5×10^{18} N/cm^3. The experimental curve is compared with the calculated line shape including the acoustic phonons contribution (1) and without phonon contributions (2). (b) The luminescence spectrum of the same crystal as in (a) excited with a low-level cw Ar^+ laser. (c) The luminescence spectrum of a low-[N] crystal excited with a cw Ar^+ laser. This spectrum is used as the phonon density of states for the line-shape calculations shown in (a).

of the radiative recombination of the excitons bound to single N (A line and its phonon sidebands) and a new band peaking at 2.302 eV. This band with its optical phonon sideband (at 2.253 eV) completely dominates the spectrum of the crystal with $[N] = 2.5\times10^{18}$ cm^{-3} [Fig. 1(a)]. Similar results are obtained when the crystals with $[N] \geq 2\times10^{17}$ cm^{-3} are excited by 2.317-eV photons, i.e., directly into the A line [Fig. 3(b)]. The dips which appear in the emission band [Fig. 1(a)] correspond to self-absorption by NN_i nitrogen pairs. This can be verified by comparing the dips energies with the NN_i emission peaks observed under cw excitation [Fig. 2(b)].

It should be noted that although the spectra were

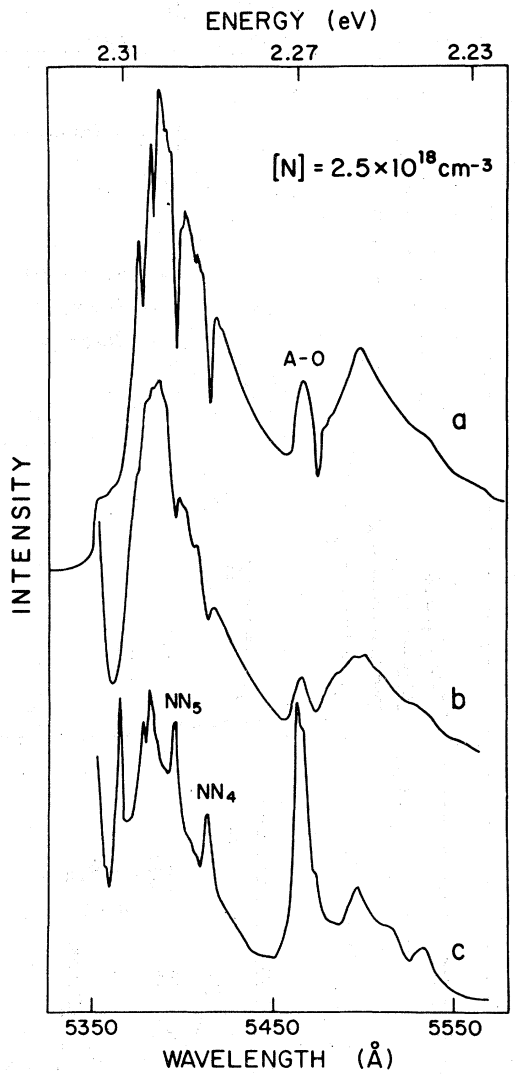

FIG. 3. (a) Electron-hole liquid radiative recombination at 2 K and exciting photon energy $h\nu = 2.65$ eV. (b) Same temperature, $h\nu = 2.317$ eV. (c) 30 K and $h\nu = 2.317$ eV. In (b) and (c) resonant A-line excitation was used and the luminescence was recorded up to 3 meV below the exciting laser line.

observed at an ambient temperature of 2 K, the local temperature at the excited region was about 5 K. This was determined by measuring the lifetime of the NN_4 line when pumping into the A line. It was observed that $\tau(NN_4) \sim 1$ μsec for all pumping intensities. Another indication of the low local temperature is obtained by comparing the 2-K spectra [Figs. 3(a) and 3(b)] with spectra taken under the same excitation conditions at higher temperatures [such as Fig. 3(c)]. The main difference is the appearance of the NN_i lines as peaks superimposed on the broad band rather than dips (the NN_i lifetime is shortened to ~40 nsec at 20 K).

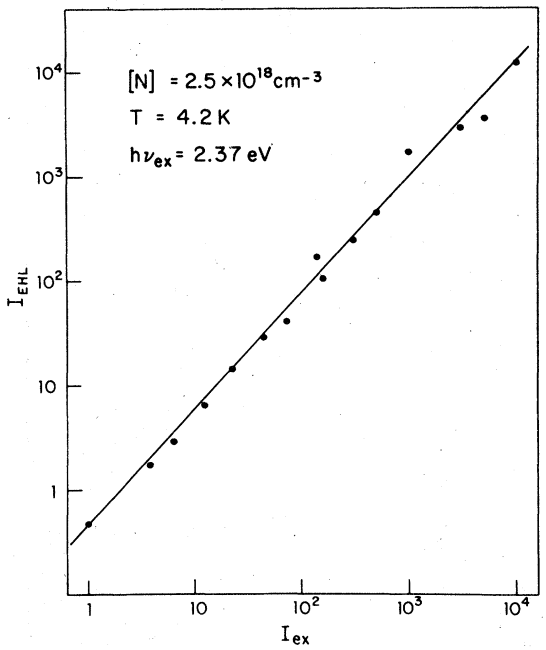

FIG. 4. Dependence of the EHL emission intensity on the intensity of the exciting laser beam.

Figure 4 shows the dependence of the integrated intensity of the broad band observed for $[N] = 2.5 \times 10^{18}$ cm^{-3} on the intensity of the exciting laser beam. (In this experiment we used a gate of 40 nsec.) The data shown are for excitation energy of 2.37 eV but similar results were obtained for 2.65- and 2.317-eV incident photons. As can be seen, the dependence is nearly linear. The spectral line shape does vary somewhat when the excitation intensity is decreased by four orders of magnitude, as is shown in Fig. 5. In order to allow a meaningful comparison between these spectra, they were all normalized to the same peak intensity at 2.302 eV.

Finally, the spectrum shown in Fig. 2(c) has been obtained by front surface excitation with a low intensity (15 mW) cw Ar^+ laser operating at 4579 Å. These experimental conditions were important in order to reduce self-absorption of the resonance A line as much as possible. Thus, the intensity ratio of the A line to its phonon sidebands could be accurately determined.

III. ANALYSIS

In this section we consider the origin of the broad emission band observed in crystals with $[N] \geq 2 \times 10^{17}$ cm^{-3} and analyze its spectral line shape. The most important observation is the possibility of exciting this band by selective excitation into the A line, i.e., by creating only excitons bound

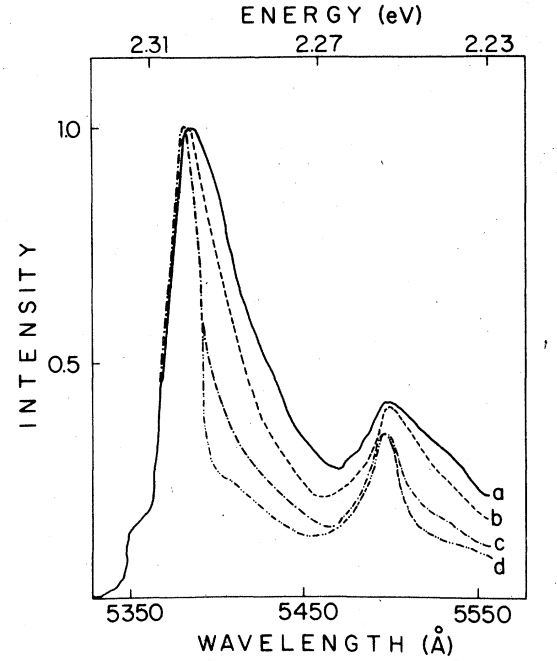

FIG. 5. Dependence of EHL recombination line shape on excitation intensity. (All spectra are normalized to the same peak intensity at 2.302 eV.) (a) 10^{18} photons/cm^2 at 2.65 eV. (b) 10^{17} photons/cm^2 at either 2.65 or 2.317 eV. (c) 10^{16} photons/cm^2 at 2.317 eV and (d) 10^{14} photons/cm^2 at 2.317 eV. In the case of A-line excitation (2.317 eV), the luminescence was recorded up to 3 meV below the exciting laser line.

to the nitrogen impurities. From this we conclude that the broad band is due to some kind of an excitonic phase within the nitrogen system. The fact that the spectra obtained by exciting deep into the conduction band are identical to those obtained under selective excitation indicates that the electron-hole pairs are trapped on the nitrogen impurities where they form the new phase. The linear dependence of the emission intensity on the excitation intensity over the range of four decades precludes the possibility of stimulated emission. Another possibility is a multiexciton complex bound to nitrogen traps, as it is well established that a biexciton can bind to a single N in GaP.[11] However, such a complex would be observed for all nitrogen concentrations while the new band is observed only for $[N] \geq 2\times 10^{17}$ cm^{-3}. This minimum nitrogen concentration corresponds to an average inter-impurity separation of 100 Å, which is roughly $2a_0$. Under this condition exciton delocalization takes place within the nitrogen system.[8] In addition, when the excitation intensity is sufficiently high and its duration shorter than τ_A, a high density of excitons is formed. The exciton separation is then of the order of a_0, and we could expect exciton condensation into an EHL. Although an EHL phase is observed also in pure GaP, there are significant differences between this case and that of GaP:N: (a) In GaP:N the high particle density is achieved via the nitrogen system, while in pure GaP the condensation is that of free excitons. (b) Since the nitrogen trap alters the electron wave function,[12] the no-phonon radiative recombination is expected to be allowed in contrast to pure GaP where only phonon assisted transitions are allowed. (c) The relative intensities of the phonon sidebands should reflect those of the GaP:N spectrum [Fig. 2(c)] rather than the free-exciton recombination spectrum as in the case of pure GaP. It should also be mentioned that the EHL formation in GaP:N differs from the cases of doped Ge and Si where the EHL is formed by condensation of free excitons.[13,14]

We have performed a line-shape analysis of the band peaked at 2.302 eV as shown in Fig. 2(a) for $[N] = 2.5\times 10^{18}$ cm^{-3}. We used the expression for the spectral density given by Pokrovskii[14]:

$$I(h\nu) = \int d(\hbar\omega) f(\hbar\omega) \int_a^b E^{1/2}(h\nu - h\nu_0 - E)^{1/2}\, dE\,.$$

Here $f(\hbar\omega)$ is the spectral line-shape function given in Fig. 2(c) for single N impurities at 4.2 K. The other symbols are defined in Ref. 14. We assumed a three-valley structure for the minimum of the conduction band and used the set of mass parameters quoted by Beni and Rice,[15] namely, $m_{\parallel} = 2.032$ and $m_{\perp} = 0.254$ for the anisotropic electron mass and $m_e = 0.164$ and $m_h = 0.479$ for the light- and heavy-hole mass, respectively. The calculated curve marked (1) in Fig. 2(a) is the result of fitting the main emission peak which consists of contributions of the no-phonon radiative recombination of the EHL and its acoustical-phonon sidebands. As can be seen, the fit is satisfactory. For comparison we also calculated the line shape of the main emission band omitting the acoustical-phonon contribution and using the same parameters obtained by the previous fitting. The result is shown in curve (2) of Fig. 2(a). The band peaked at 2.253 eV lies 49 meV below the peak of the no-phonon EHL peak and thus corresponds to its optical-phonon sideband. We have calculated its line shape, again using $f(\hbar\omega)$ given in Fig. 2(c). While the calculated line shape fits well the experimental curve, its intensity turns out to be 50% stronger than that observed experimentally. A possible explanation might be the different coupling of the TO and LO phonons to the EHL.

The experimental value of the binding energy of the EHL is 17 meV with respect to the free-exciton line (accurately determined from the position of the A_x line[4]). This value is close to the estimates of Beni and Rice.[15] The binding energy is some-

TABLE I. Electron-hole liquid parameters as a function of the excitation intensity.

Excitation intensity (photons/cm^2/pulse)	10^{18} [a]	10^{17}	10^{16}	10^{14}
Electron-hole pair density (10^{18} cm^{-3})	4.1	3.3	2.4	1.5
$E_e^F + E_h^F$ (meV)	26	22	18	13
τ (nsec)	15	30	35	38

[a] In this case the excitation energy was 2.65 eV, while in all other cases resonant A-line excitation was used.

what larger than that of the EHL in pure GaP (14 meV).[1] This effect is probably due to the additional attraction of the electrons by the nitrogens.

A similar line-shape analysis was performed for the EHL in the crystal with $[N] = 2.5 \times 10^{18}$ cm^{-3} obtained under excitation intensities varying from 10^{14} to 10^{18} photons/cm^2 per pulse (data of Fig. 5). The results are summarized in Table I. For a four orders of magnitude change in the excitation flux, the density of particles in the EHL varies only slightly. (The density is calculated from the Fermi energies of electrons and holes determined by the fit to the experimental data.) In all cases the density of particles in the EHL is of the same order of magnitude as the concentration of nitrogen impurities. This means that even for the lowest excitation intensity for which the EHL radiative recombination is observed the excitons migrate within the nitrogen system and concentrate in regions which, consequently, have a high density of particles. The observed binding energy of the EHL does not vary with the excitation intensity. This is in agreement with the calculations of Beni and Rice[15] which indicate that it varies only slightly with small changes in the electron-hole density.

Table I also includes the radiative lifetime of the EHL for the different excitation intensities. This lifetime depends on the density, and in all cases is shorter than τ_A. This shows the importance of the Auger effect in determining the lifetime. It should be noted that the biexciton lifetime is less than 10 nsec,[11] which means that the particles overlap much more in the biexciton than in the EHL.

Finally, an additional support to the model presented here can be found in the A-line absorption saturation experiments reported by Leheny and Shah.[16] They have shown that in crystals containing $[N] \geq 5 \times 10^{17}$ cm^{-3} the A-line absorption saturates for pumping intensity greater than 10^{16} photons/cm^2 per pulse. For the highest available pumping intensity a net amplification of 8.5 was expected but none observed. From this they have concluded that the excited nitrogen system is in an excited state unattainable by direct absorption from the ground state. This state is the condensed EHL formed by populating all the nitrogen impurities with excitons. Clearly a model which assumes that the nitrogen impurities simply induce the no-phonon transition of the conventional EHL (formed from free excitons) cannot explain these absorption saturation experiments.

IV. SUMMARY

In this paper we have demonstrated the formation of an EHL by the condensation of excitons bound to nitrogen in GaP:N. This EHL is formed when the average separation between nitrogen impurities is of the order of the exciton Bohr radius and when the density of electron-hole pairs is of the same order of magnitude as the nitrogen concentration. The role of the nitrogen dopants is twofold: it provides the particles for the EHL and it determines the spectral line shape of its radiative recombination.

ACKNOWLEDGMENT

The technical assistance of H. Katz and S. Shirazi is greatly appreciated.

[1] J. Shah, R. F. Leheny, W. R. Harding, and D. R. Wight, Phys. Rev. Lett. 38, 1164 (1977).
[2] H. Maaref, J. Barrau, M. Brousseau, J. Collet, and J. Mazzaschi, Solid State Commun. 22, 593 (1977).
[3] D. Hulin, M. Combescot, N. Bontemps, and A. Mysyrowicz, Phys. Lett. 61A, 349 (1977).
[4] D. G. Thomas and J. J. Hopfield, Phys. Rev. 150, 680 (1966).
[5] M. D. Sturge, E. Cohen, and K. F. Rodgers, Phys. Rev. B 15, 3169 (1977).
[6] R. Schwabe, F. Thuselt, R. Bindemann, W. Seifert, and K. Jacobs, Phys. Lett. 64A, 226 (1977).
[7] We use the free-exciton Bohr radius as an estimate for that of the exciton bound to nitrogen.
[8] Evidence of exciton delocalization in crystals with $[N] \geq 5 \times 10^{17}$ cm^{-3} is provided by energy-transfer experiments reported by P. J. Wiesner and R. A. Street [J. Lumin. 12–13, 265 (1976)].
[9] J. D. Cuthbert and D. G. Thomas, Phys. Rev. 154, 763 (1976).
[10] The crystals were grown at Bell Laboratories by C. J. Frosch and R. T. Lynch. Apart from nitrogen, the background impurity concentration was less than 10^{16} cm^{-3}. All were bulk doped except for the sample with

$[N] = 5 \times 10^{16}$ cm^{-3} in Fig. 1 which has an epilayer 70-μm thick.
[11]J. L. Merz, R. A. Faulkner, and P. J. Dean, Phys. Rev. 188, 1228 (1969).
[12]P. J. Dean, J. Lumin. 12, 398 (1970).
[13]R. W. Martin, Phys. Status Solidi B 66, 627 (1974).
[14]Y. Pokrovskii, Phys. Status Solidi A 11, 385 (1972).
[15]G. Beni and T. M. Rice, Solid State Commun. 23, 871 (1977).
[16]R. F. Leheny and J. Shah, Phys. Rev. B 12, 3268 (1975).