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Nitrogen Concentration in GaP:N Epitaxial Layers
from Localized Mode Absorption Measurements

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The doping of GaP epitaxial layers with nitrogen is of considerable interest in optoelectronic applications. A simple non-destructive method widely used to evaluate the nitrogen doping level in GaP is to measure the integrated absorption of the so-called A-line associated with the direct creation of excitons bound to isolated nitrogen atoms without phonon cooperation /1, 2/. However, at nitrogen concentrations $N_N \approx 10^{19} \text{ cm}^{-3}$ this method becomes rather inaccurate because of the occurrence of intense competing absorption processes from NN_1 pairs /2, 3/. Recently, it has been found that one possibility to overcome these difficulties arising at high nitrogen doping levels is the determination of N_N from the lattice parameter change caused by the incorporation of nitrogen atoms into the GaP lattice /2, 4/. In the present communication it is shown that optical absorption measurements at the nitrogen-induced localized vibrational mode can be also successfully employed to determine N_N in GaP:N epitaxial layers up to the highest nitrogen doping levels reported so far.

The samples used in the measurements were GaP:N vapour phase epitaxial layers deposited onto (111) oriented GaP substrates. The substrate thickness d_s was in the range from 100 to 150 μm , the thickness d_f of the layers varied between 15 and 40 μm . The nitrogen concentration in samples with $N_N \lesssim 10^{19} \text{ cm}^{-3}$ was determined using the A-line absorption method as described in detail in /1, 2/. In samples with higher nitrogen concentrations the N_N values were either estimated from the NH_3 flow rate during growth or by precision lattice parameter measurements using the results of /2, 4/. For our measurements we selected seven samples with N_N values between 2×10^{17} and $3 \times 10^{19} \text{ cm}^{-3}$, the parameters of these samples are given in Table 1.

To determine the optical absorption coefficient $\alpha_N(\bar{\nu})$ due to the nitrogen-induced localized vibrational mode located at $\bar{\nu}_{\text{loc}} = 495 \text{ cm}^{-1}$ /5, 6/ we meas-

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Table 1

Parameters of the GaP:N epitaxial layers

sample	$d_f(\mu\text{m})$	$N_N(10^{18} \text{ cm}^{-3})$	$\bar{\nu}_{\text{loc}}(\text{cm}^{-1})$	$\alpha_{N\text{max}}(\text{cm}^{-1})$	$\Delta\bar{\nu}(\text{cm}^{-1})$
1	17.0	0.2	494.0	4.5	7.0
2	31.6	0.8	494.5	20	7.0
3	34.6	1.5	494.2	38	8.0
4	18.6	2.9	494.5	63	6.5
5	21.0	5.9	494.5	118	8.0
6	18.6	10.5	494.5	328	6.2
7	20.4	30	494.5	820	6.0

ured the optical transmittance spectra $T(\bar{\nu})$ of the samples at room temperature in the wave-number range $\bar{\nu} = 400$ to 600 cm^{-1} at normal incidence of the radiation using a Perkin-Elmer spectrophotometer model 580B. Now, in evaluating $\alpha_N(\bar{\nu})$ from the measured transmittance $T(\bar{\nu})$ it must be taken into account that in this wave-number range intrinsic two-phonon transitions /7/ and, in general, also free carriers in both the substrate and the layer contribute to the absorption. Accounting for this fact and assuming the same value of the refractive index n for the substrate and the film the transmittance T of the GaP:N/GaP film-substrate system is given by

$$T = \frac{(1 - R)^2 \exp(-\beta)}{1 - R^2 \exp(-2\beta)} \quad (1)$$

with

$$\beta = \alpha_s d_s + \alpha_f d_f, \quad (2)$$

where $\alpha_s = \alpha_p + \alpha_{cs}$ and $\alpha_f = \alpha_p + \alpha_{cf} + \alpha_N$ are the absorption coefficients of the substrate and the layer, respectively, α_p and α_c are the absorption coefficients due to two-phonon transitions and free carriers, and $R = [(n - 1)/(n + 1)]^2$ is the reflectivity. Thus, to calculate $\alpha_N(\bar{\nu})$ from the measured $\beta(\bar{\nu})$ the knowledge of the contributions $\beta_p = \alpha_p(d_s + d_f)$ due to two-phonon transitions and $\beta_c = \alpha_{cs}d_s + \alpha_{cf}d_f$ due to free carriers to β must be known. The absorption spectrum $\alpha_p(\bar{\nu})$ due to two-phonon transitions is independent of the specific sample and can, in principle, be taken from the literature /7/. To be

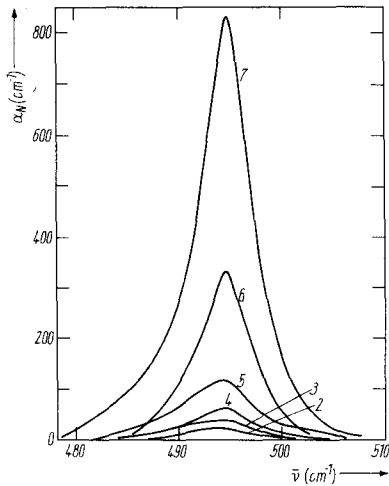
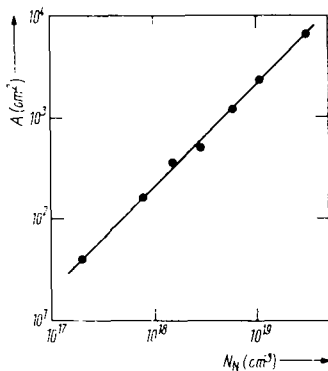


Fig. 1. Nitrogen-induced localized mode absorption bands in GaP:N epitaxial layers with different nitrogen concentrations. The notation of the samples is the same as in Table 1

sufficiently accurate in evaluating α_N we have determined $\alpha_p(\bar{\nu})$ in the frequency range of interest by independent measurements on undoped GaP single crystals. Contrary to α_p , the absorption coefficients $\alpha_{cs}(\bar{\nu})$ and $\alpha_{cf}(\bar{\nu})$ due to free carriers depend on the doping level with electrically active impurities and, therefore, differ from sample to sample. However, since $\alpha_{cl}(\bar{\nu})$ are always monotonous functions of $\bar{\nu}$ the contribution β_c to β in the range of the localized mode can be determined by measuring $\beta(\bar{\nu})$ in the wave-number ranges well below and above the localized mode frequency where $\alpha_N = 0$, subtracting β_p from the measured β , and then interpolating between two parts of the $\beta_c(\bar{\nu})$ curve obtained in this manner. In our experiments we found that measurements in the wave-number range $\bar{\nu} = 450$ to 550 cm^{-1} are sufficient to determine all the quantities required.

The resulting absorption spectra $\alpha_N(\bar{\nu})$ due to the nitrogen-induced localized vibrational mode for the samples 2 to 7 are represented in Fig. 1, the peak position $\bar{\nu}_{loc}$, the maximum absorption coefficient α_{Nmax} , and the half-width $\Delta\bar{\nu}$ of the absorption line of all the samples are compiled in Table 1. Fig. 2 shows a double-logarithmic plot of the integrated absorption



$A = \int \alpha_N(\bar{\nu}) d\bar{\nu}$ of the nitrogen-induced absorption bands against the nitrogen concentration N_N . An analysis of the data shows that the dependence of A on N_N follows a linear relation $A = A_0 N_N$ (full line in Fig. 2) with $A_0 = (2.07 \pm 0.01) \times 10^{-16} \text{ cm}$ over the whole concentration range considered. Furthermore, it can be seen from Table 1 that

Fig. 2. Plot of the integrated absorption against the nitrogen concentration

the width $\Delta\bar{\nu}$ at half height of the absorption bands has approximately the same value of $\Delta\bar{\nu} = (7 \pm 1) \text{ cm}^{-1}$ for all samples. Because of $A \sim \alpha_{N\text{max}} \Delta\bar{\nu}$ this means that N_N can be also determined from the maximum absorption coefficient at $\bar{\nu} = \bar{\nu}_{\text{loc}}$. Assuming $\alpha_{N\text{max}} = a_0 N_N$ we find for the proportionality constant a value of $a_0 = (2.40 \pm 0.15) \times 10^{-17} \text{ cm}^2$.

Thus, we see that the optical absorption measurement at the nitrogen-induced localized vibrational mode provides another possibility to determine the nitrogen concentration in GaP epitaxial layers, in particular at high N_N values where, firstly, the A-line absorption method fails and, secondly, the absorption coefficients α_N become high and well distinguishable from the competing absorption due to two-phonon transitions and free carriers. However, it should be noted that the parameters A_0 and a_0 found in our experiments are only valid for room temperature. As it follows from theoretical considerations /9/ the integrated absorption A of a localized mode induced by an impurity with mass M and concentration N can be written as

$$A = \frac{(\eta e)^2 N}{4 \epsilon_v c^2 n M} \quad , \quad (3)$$

where ϵ_v is the permittivity of free space, c the vacuum velocity of light, n the refractive index of the host crystal, and ηe the so-called apparent charge characterizing the oscillator strength of the impurity-induced absorption process. From our room temperature data we find an apparent charge of $\eta = 4.27$ whilst a value of $\eta = 1.4$ has been reported for 77 K /10/. Therefore, since it follows from relation (3) that $A_0 \sim \eta^2$, a decrease of A_0 with decreasing temperature must be expected.

In conclusion, we note that the frequency of the localized mode found here is below the frequencies $\bar{\nu}_{\text{loc}} = 495.8$ to 496.1 cm^{-1} reported for 77 K /5, 10/. Assuming $\bar{\nu}_{\text{loc}}(300 \text{ K}) = 494.5 \text{ cm}^{-1}$ (see Table 1) and accounting for the thermal expansion behaviour of GaP in the temperature range from 77 to 300 K /11/, the corresponding mode Grüneisen parameter $\gamma_{\text{loc}} = -d(\ln \bar{\nu}_{\text{loc}})/d(\ln V)$ can be calculated. We find a value of $\gamma_{\text{loc}} = 1.3 \pm 0.1$ which agrees with the mode Grüneisen parameters of the fundamental optical modes of GaP which are in the range $\gamma = 1.1$ to 1.5 /12/.

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