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# CHANGES OF GaP : N DEFECT STRUCTURE UNDER HYDROSTATIC PRESSURE

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Dedicated to Professor Dr. Julian Auleytner
on the occasion of his 70th birthday

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The changes of defect structure of GaP:N epitaxial layers subjected to hydrostatic pressures up to 1.8 GPa are investigated by X-ray diffraction and photoluminescence. The observed changes are more pronounced at higher pressures and depend on the nitrogen concentration, $c_N$, and on initial defect structure. Especially complex hydrostatic pressure induced properties are observed for the sample with $c_N > 10^{20}$ at. cm$^{-3}$. The model explaining the hydrostatic pressure induced defect structure changes is proposed.

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## 1. Introduction

It has been established [1, 2] that single-crystalline Si and GaAs containing inhomogeneities of different compressibility, as compared to that of the matrix, can change defect structure under hydrostatic pressure (HP). This effect is due to the stress at the precipitate/matrix boundary caused by HP; above the critical stress some additional defects, which stretch the crystal lattice, could be created.

The GaP:N crystal is even more interesting for HP investigations because of reported discordant information concerning the maximum obtainable nitrogen concentration and complicated defect structure of GaP heavily doped by nitrogen.

The GaP:N epitaxial layers with the total nitrogen concentration, $c_N$, up to above $10^{20}$ at. $cm^{-3}$ were produced by vapour phase epitaxial chemical vapour deposition (VPE CVD) method [3]. On the other hand, the direct synthesis from liquid GaP and gaseous nitrogen at HP, pressure up to 1.8 GPa and temperature up to 1730 K, made it possible to reach the concentration of optically active nitrogen not exceeding $3 \times 10^{19}$ at. $cm^{-3}$ [4, 5].

Let us mention that doped GaP epitaxial layers are widely used in optoelectronics for the production of luminescence diodes emitting green-yellow light. Nitrogen as an isoelectronic dopant has a strong effect on the quantum efficiency of the light emission. The intensity of the emitted light is directly proportional to $c_N$, up to $1.5 \times 10^{19}$ at. $cm^{-3}$.

In GaP:N single crystals the lattice parameter decreases linearly with $c_N$ at least up to $c_N = 3.3 \times 10^{19}$ at. $cm^{-3}$ [6]. In the case of higher $c_N$, like for the samples with $c_N \geq 10^{20}$ at. $cm^{-3}$, the lattice parameter increases with $c_N$, while the luminescence intensity decreases [3]. At such high concentrations the nitrogen atoms create split interstitial pairs and, as a result, the electron trap ($T_3$ level) concentration increases [7].

## 2. Experimental

The GaP and GaP:N ($c_N = 1.35 \times 10^{19}$ at. $cm^{-3}$ and $c_N \geq 10^{20}$ at. $cm^{-3}$) epitaxial layers of 10 to 30 $\mu$m thickness, deposited by VPE CVD method on the (100) GaP substrate [3], were subjected to pulsating ($n$ = 1, 3, 6 and 12 cycles) quasi-hydrostatic pressure treatment (between 0.1 GPa and maximum applied pressure equal to 1.3 or 1.8 GPa) in $n$-isopentane.

The initial (HP untreated) samples indicated high concentration (at least $10^5$ $cm^{-3}$) of almost unresolvable defects (dislocations or small precipitates) as determined by X-ray topography [3]. The same was observed after the HP treatment.

The samples were investigated by the Bond method (determination of the lattice constant and linear thermal expansion coefficient values), double crystal spectrometry (determination of the rocking-curve half-width $\Delta\Theta$) and X-ray topography.

The photoluminescence spectra of the samples were obtained at 10 K with the aid of experimental setup described in [8]. The excitation was accomplished by a HBO 200 mercury lamp ($\lambda$ = 365 nm). The emission was detected using a photon counting technique.

## 3. Results

Defect structure changes, observed in the HP treated GaP:N single crystals, become more pronounced for the higher pressure and the higher number of pressure cycles (for one cycle, i.e. static pressure, the changes do not occur).

For the undoped sample ($c_N = 0$) no structure changes are observed even after the treatment at the highest applied pressure and 12 pressure cycles.

The lattice constant value of GaP:N ($c_N = 1.35 \times 10^{19}$ at. $cm^{-3}$) samples HP treated at $p = 1.8$ GPa is lower than that of the HP untreated, depending on

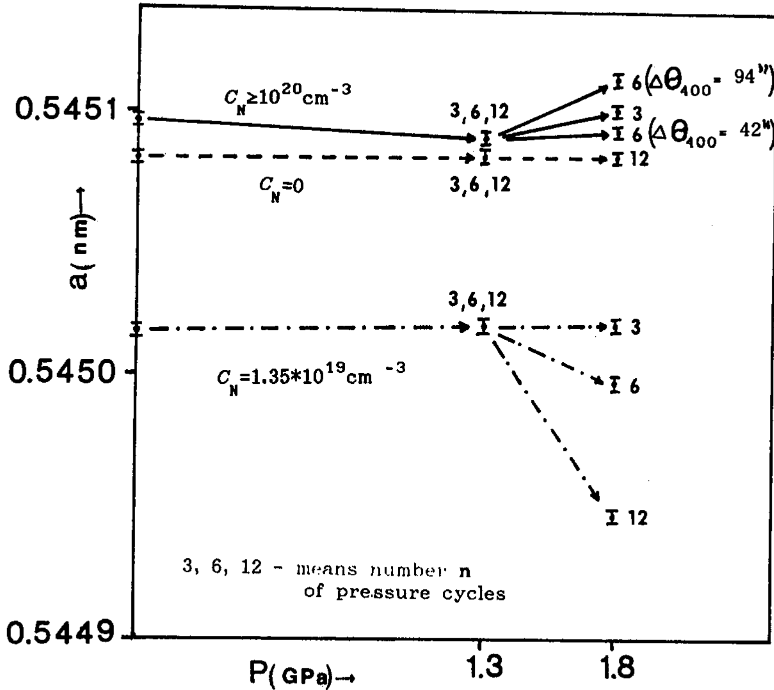



Fig. 1. The lattice constant $a$ determined for the GaP:N samples subjected to HP. Different values of $a$ for the sample with $c_N > 10^{20}$ at. cm$^{-3}$ ($p = 1.8$ GPa, 6 cycles) correspond to different positions at the sample ($x = 0$ and 3 mm, Fig. 2). The error of $a$ is $\pm 2 \times 10^{-6}$ nm.

the number of pressure cycles (Fig. 1). The HP treatment does not influence the value of $\Delta\Theta_{400}$.

The properties of the HP treated GaP:N sample with $c_N > 10^{20}$ at. cm$^{-3}$ are more complex and depend on the local defect concentration. The lattice constant decreases slightly for the sample HP treated at 1.3 GPa but rises markedly in the case of higher pressure treatment (Fig. 1). This rise depends on the primary defect concentration in the sample. Simultaneously, the $\Delta\Theta_{400}$ value also increases (Fig. 2). Furthermore, the changes of appearance of this sample depend on the primary defect concentration; whereas the part I with the lower lattice constant and $\Delta\Theta$ values seems to be unchanged, the part II with the higher lattice constant and $\Delta\Theta$ values becomes distinctly darker. The value of thermal expansion coefficient is lower for the part II of the crystal than for the part I ($4.85 \times 10^{-6}$ K$^{-1}$ and $5.05 \times 10^{-6}$ K$^{-1}$, respectively).

The observed changes are related to the photoluminescence spectra (Figs. 3 and 4). The resolved sharp lines are observed for the HP treated sample with $c_N = 1.35 \times 10^{19}$ at. cm$^{-3}$ and for part I of sample with $c_N \geq 10^{20}$ at. cm$^{-3}$. Photoluminescence spectra of initial samples are much broader.

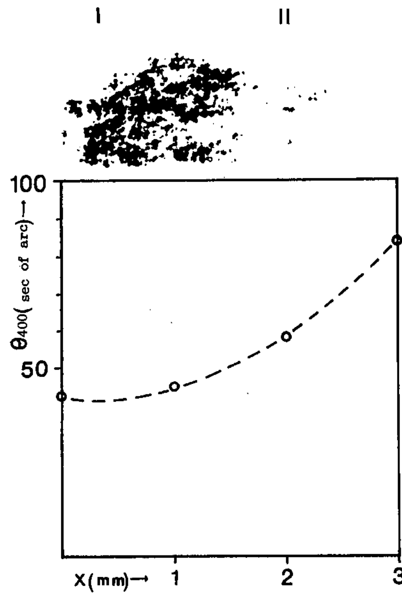



Fig. 2. The rocking-curve half-width $\Delta\Theta$ for 400 reflection measured along the GaP:N sample with $c_N > 10^{20}$ at. $cm^{-3}$ subjected to HP 6 cycles up to 1.8 GPa. The X-ray transmission topograph of the sample is presented.

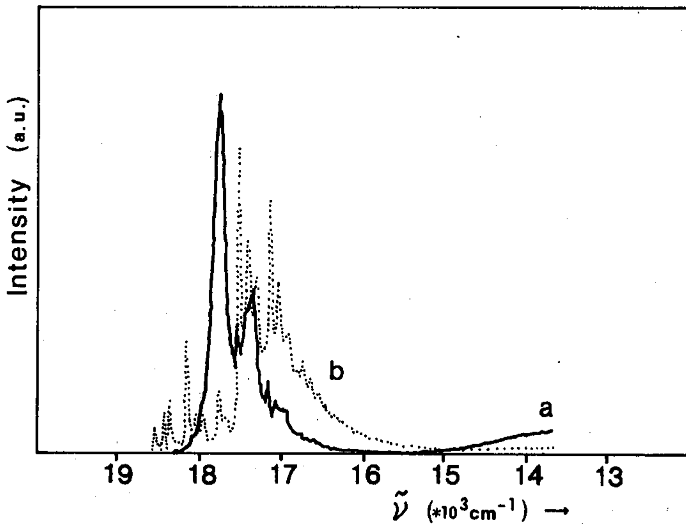



Fig. 3. Photoluminescence spectra taken at 10 K of the GaP:N sample with $c_N = 1.35 \times 10^{19}$ at. $cm^{-3}$: *a* — HP untreated sample; *b* — after HP treatment at 1.8 GPa, 12 cycles. The spectrum *b* consists of a series of sharp lines resulting from the creation of exciton bound on the substitutional atom pairs ($NN_1$, $NN_3$) and their phonon replicas.

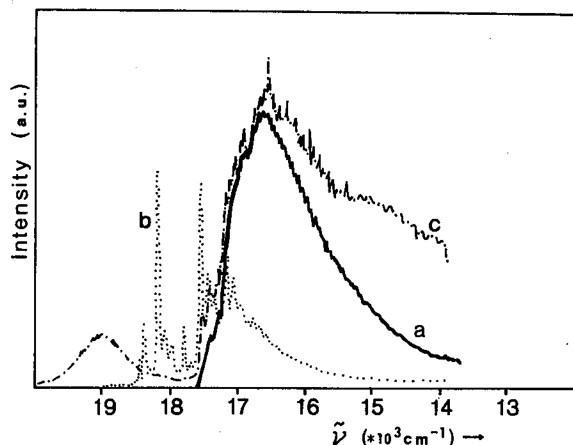



Fig. 4. Photoluminescence spectra taken at 10 K of the GaP:N sample with $c_N > 10^{20}$ at. cm$^{-3}$: *a* — HP untreated sample; *b*, *c* — after HP treatment at 1.8 GPa, 6 cycles. The spectra *b* and *c* are determined at the I and II positions (Fig. 2) on the crystal. The spectrum *b* consists, except for the $NN_1$, $NN_3$ lines and their phonon replicas, also of the *A* line corresponding to exciton bound on the substitutional nitrogen atom.

## 4. Discussion

The HP treatment changes distinctly the properties of GaP:N, contrary to the lack of any changes in undoped GaP. The observed effects are more pronounced for both higher pressure and number of cycles. They depend on $c_N$ and are related to the sample defect structure.

The lattice constant of the untreated sample with $c_N = 1.35 \times 10^{19}$ at. cm$^{-3}$ is lower than that of undoped GaP. It means that the nitrogen atoms occupy mostly the phosphorus positions [6]. It does not exclude, however, that some of the nitrogen atoms occupy also the interstitial positions or form split interstitial pairs. The photoluminescence spectrum of the sample is broad (Fig. 3) due to the stresses existing in the lattice.

The HP treatment leads to the decrease in lattice constant (Fig. 1). The observed photoluminescence spectrum is of better resolved structure (Fig. 3) — the concentration of optically active nitrogen (in the lattice positions) and the lattice strain decrease. This effect is unusual, as one would rather expect a rise of lattice constant and of the strains in the case of HP treated semiconductor [1].

The observed behaviour is expected to be due to the distribution of nitrogen atoms in different sites. In the GaP:N samples with higher $c_N$ the nitrogen atoms are located in the crystal lattice as:

a) substitutional atoms, $N_s$, nitrogen atoms at the lattice positions of phosphorus atom. It results in a decrease in the lattice constant as compared to that of stoichiometric GaP [6] (nitrogen atomic radius, $r_N$, is smaller than that of phosphorus: 0.053 nm and 0.108 nm, respectively);

b) split interstitial pairs of nitrogen atoms, $N_p$ (corresponding to $T_3$ level). It causes the rise of the lattice constant [3];

c) interstitial nitrogen atoms, $N_i$. Such a configuration is unstable but nevertheless possible for "nitrogen oversaturated" crystal [7]. The influence of $N_i$ concentration, $c_{N_i}$, on the lattice constant is not known. It seems, however, that the rise of $c_{N_i}$ would influence the lattice parameter only slightly, because the radius of the tetrahedral interstitial site in GaP (about 0.105 nm) is much larger than that of the nitrogen atom;

d) larger nitrogen agglomerates at the dislocation core and clusters containing also other atoms [9, 10].

As the result of pulsating HP treatment some of the substitutional nitrogen atoms ($N_s$) and dissociated split interstitial pairs ($N_p$) move to the interstitial sites and/or to the dislocation cores [7, 9], just nearby the initial position of nitrogen atom. The HP treatment was performed at the room temperature and the pronounced diffusion of nitrogen is not probable.

The sample with $c_N \geq 10^{20}$ at. cm$^{-3}$ is "nitrogen oversaturated" with high concentration of $N_p$ and $N_i$ as well as of the larger, nitrogen containing defects. The presence of these all mentioned above defects is confirmed by an increase in lattice constant [3]. A broad, unresolvable photoluminescence spectrum (Fig. 4) as well as X-ray topography (Fig. 2) indicate a considerable stress of the lattice.

The change of appearance of the different parts of the HP treated samples as well as of their photoluminescence spectra (Fig. 4) are related to the defect structure as detected by X-ray topography and the rocking-curve half-width (Fig. 2). The photoluminescence spectrum of the part II with the higher concentration of defects remains unresolved after HP treatment (Fig. 4); the lattice constant increases. It indicates that the stresses in the sample increase after HP treatment.

It seems that in the above case the process of formation of additional defects at the boundary between the initially existing defect (e.g. Ga inclusion) and the GaP matrix dominates. It is much more pronounced than for the case of sample with $c_N = 1.35 \times 10^{19}$ at. cm$^{-3}$ because of higher concentration of initially existing defects.

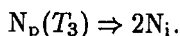
The above conclusion is supported by the behaviour of the part I of the same sample with the lower concentration of primary defects (Fig. 2). Few additional defects are formed under HP. After HP treatment at 1.8 GPa the lattice constant remains almost unchanged whereas the photoluminescence spectrum is well resolved (Fig. 4). The line $A$ from substitutional nitrogen $N_s$ is observed. It follows that the concentration of optically active nitrogen is even lower than that in the HP treated sample with $c_N = 1.35 \times 10^{19}$ at. cm$^{-3}$. Furthermore, it means that the process of $N_p$ and $N_s$ removing from their primary positions takes place also for the samples with the highest nitrogen concentration.

## 5. Conclusions

As the result of pulsating HP treatment at higher pressures the dramatic changes of the GaP:N defect structure occur. At least two phenomena are observed.

The first one is the creation of additional defects at the boundary between the GaP matrix and defects (e.g. Ga precipitates) of different compressibility.

The second one relates to the nitrogen atoms incorporated in the lattice. There is an evidence that some of the nitrogen atoms are removed from the original lattice sites and that the split interstitial pairs of nitrogen atoms $N_p$ dissociate into the $N_i$ interstitials, according to



$$N_p(T_3) \Rightarrow 2N_i.$$

Such changes of the defect structure can be considered as an "improvement" of the general crystal lattice perfection manifested by the decrease in the lattice constant and the sharpening of the photoluminescence spectrum.

On the other hand, the formation of additional defects (the first mentioned above phenomenon) occurs simultaneously. It is especially pronounced for the sample with $c_N \geq 10^{20}$ at. cm$^{-3}$. Creation of additional defects causes the increase in the lattice constant and in the rocking-curve half-width as well as broadening of the photoluminescence spectra.

The observed decrease in the substitutional nitrogen atoms concentration in the HP treated samples is in agreement with the results of the previous studies [4, 5, 11] which concluded that the nitrogen solubility in the GaP lattice under HP conditions is limited.

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