Exciton-Phonon Coupling of NN_3 Center in Heavily Nitrogen Doped GaP*

Gao Yulin[1], Lü Yijun[1], Zheng Jiansheng[1], Zhang Yong[2], A. Mascarenhas[2], H. P. Xin[3] and C. W. Tu[3]

(1 *Department of Physics, Xiamen University, Xiamen 361005, China*)
(2 *National Renewable Energy Laboratory, Golden, USA*)
(3 *Department of Electrical and Computer Engineering, University of California, USA*)

Abstract: Under heavy nitrogen doping, due to the "concentration quenching" effect, the full spectrum of the NN_3 center is revealed without the interference from the spectra of other higher energy centers. This investigation offers a direct proof for that all the phonon replicas are the phonon sidebands governed by the Huang-Rhys' multiphonon optical transition theory.

Key words: GaPN; photoluminescence; isoelectronic impurity
PACC: 7280E; 7855E; 7865K
CLC number: O472.3 **Document code**: A **Article ID**: 0253-4177(2004)08-0889-05

1 Introduction

The emission spectrum of nitrogen centers have been investigated for several decades since Thomas *et al.*[1] showed that a series of sharp lines in GaP:N were the results of the radiative decay of excitons bound to either isolated nitrogen centers or various nitrogen pair centers (NN_i). NN_i^*, always appearing as a doublet and accompanying each NN_i, is the phonon replica related to the optical phonons. Although this system has been studied intensively and extensively in the dilute nitrogen doping limit[2~4], the assignments for the detailed spectral features still remain controversial, especially for some features involving phonons. A clear understanding toward the origins of their phonon replicas can give valuable insights to the characters of these isoelectronic impurity centers. It has been demonstrated that the phonon related spectroscopy structure of NN_1 exhibits a great similarity with that of the isolated center, except that NN_1 has an extra replica due to the nitrogen local mode. However, the comparison of any other nitrogen pair (NN_i with $i \geq 3$) with the isolated N center is ambiguous because of the overlapping of the spectral features from different nitrogen pairs. Essentially, the complication is due to the fact that the difference in their zero phonon line energies is typically smaller than the optical phonon energy. An interesting issue was raised in the 1980's: whether this NN_i^* is just a usual phonon side band of NN_i as described by the well-known theory of Huang and Rhys[5]. For example, it was reported[6] that NN_i^* had a totally different temperature dependence from NN_i and exclaimed that NN_i^* and

* Project supported by National Natural Science Foundation of China (No. 60276002), and Pre-Research Foundation of Xiamen University (No. Y07005)

Gao Yulin female, was born in 1969, PhD. She is engaged in the research on optical properties of III-V semiconductors.

Received 13 November 2003, revised manuscript received 10 February 2004

NN_i are independent centers. However, it was later pointed out by Zheng *et al*.[7] that the abnormal temperature dependence was due to errors in tracing the temperature evolution of NN_i^* ($i = 4 \sim 6$) exactly due to the overlapping spectra of the different NN_i centers, which was further confirmed by the selective excitation study of Zhang *et al*.[8] Nevertheless, the temperature dependence of the full spectrum of the NN_3 center has not been examined directly. Beside the selective excitation, in principle, there is the other way to isolate the spectrum of NN_3 from the rest of higher energy pairs, that is, using the effect of the "concentration quenching". With increasing nitrogen concentration, it has been found that due to the energy transfer from shallow to deep bound states, the NN_i emission quench sequentially in the order of decreasing the index i. However, the traditional growth techniques such as LPE and VPE could not reach high enough nitrogen concentration to have the emission from all the centers with $i > 3$ quenches. Fortunately, now with the improvement in the material growth, the nitrogen concentration as high as $10^{19} \sim 10^{21}cm^{-3}$ can be readily obtained by using the techniques like metalorganic vapor-phrase epitaxy (MOVPE)[9] and molecular beam epitaxy (MBE)[10,11]. In this paper, we have investigated the photoluminescence of NN_3 center with all its phonon replicas resolved without the interference of any other centers in heavily doped GaP(often referred to as GaPN). This study unambiguously confirms that the NN_i^* is phonon sidebands in the normal sense, and the NN_3 has the same phonon sideband structure of NN_1.

2 Experiment

The $GaP_{1-x}N_x$ samples were grown on (100) GaP substrates by MBE. The epilayer thickness was 250nm, with a 200nm GaP buffer. More detailed descriptions for the samples can be found in a previous publication[12]. The sample was placed in the ample cell of CSA-202E refrigerator. The temperature was varied from 19K to 48K. The excitation source was the 488nm line of an Ar^+ laser with a power about 10mW. The luminescence from the sample was dispersed by a GDM-1000 grating double monochrometer and detected by a cooled C31034 photomultiplier and a PAR124A lock-in amplifier.

3 Results and discussion

Figure 1 is a photoluminescence spectrum of GaP:N with nitrogen concentration [N] = $2.4 \times 10^{18}cm^{-3}$ under above gap excitation[6], where NN_i^* represents the doublet feature associated with optical phonons (NN_i-LO^{Γ} and NN_i-X). For the samples with moderate nitrogen concentrations, the PL spectra are usually dominated by NN_i centers with high index i and their phonon sidebands as shown in Fig. 1. One can see that it is rather crowded in the region of $18000 \sim 18200cm^{-1}$ which composes of the phonon sidebands of $NN_4 \sim NN_7$ as well as NN_3. However, as shown in Fig. 2, when the nitrogen concentration reaches $x = 0.12\%$ (or [N] = $3.0 \times 10^{19}cm^{-3}$) for $GaP_{1-x}N_x$, due to a very effective exciton transfer process[13], emission from all the NN_i centers with $i > 3$ has diminished. Thus, a clean spectrum of the NN_3 center is revealed. Figures 3 and 4 show the photoluminescence spectra of the sample $GaP_{1-x}N_x$ with $x = 0.12\%$ ([N] = $3.0 \times 10^{19}cm^{-3}$) at different temperatures from 19K to 48K, in which LO is the doublet of NN_3^* that can no longer be resolved due to the line width broadened.

According to the multiphonon optical transition theory[11], the transition probability of optical transition between initial and final electronic states accompanied by the emission of p phonons of $\hbar\omega$ is

$$F_p = |M_{ij}|^2 \left(\frac{\bar{n}+1}{\bar{n}}\right)^{p/2} e^{-S(2\bar{n}+1)} I_p\left(2S\sqrt{\bar{n}(\bar{n}+1)}\right) \quad (1)$$

where p is the number of the phonons, I_p is a Bessel function of order p and imaginary argument, S is the so-called Huang-Rhys factor, $\bar{n}$ is the

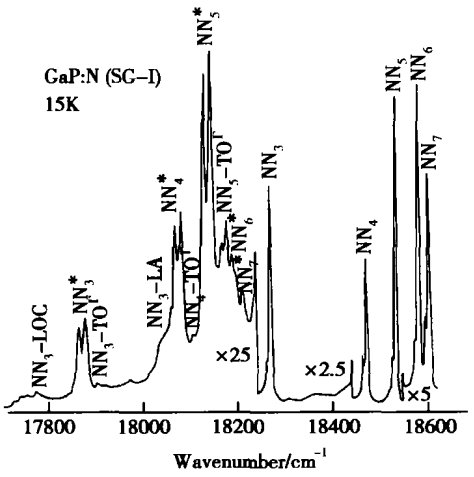

Fig. 1 Photoluminescence spectra of GaP∶N with low nitrogen concentration

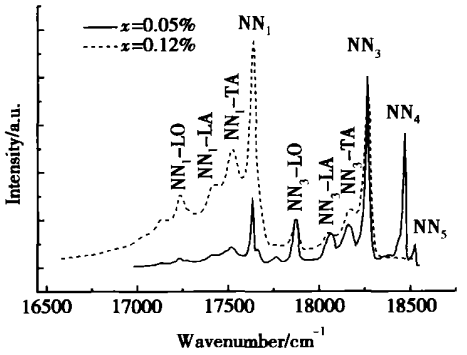

Fig. 2 Photoluminescence spectra of $GaP_{1-x}N_x$ (x = 0.05%, 0.12%) at 19K

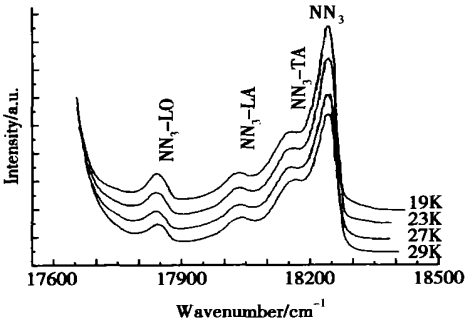

Fig. 3 Photoluminescence spectra of $GaP_{1-x}N_x$ (x = 0.12%) at 19～29K

statistical average phonon number:

$$\bar{n} = \frac{1}{e^{\hbar\omega/kT} - 1} \tag{2}$$

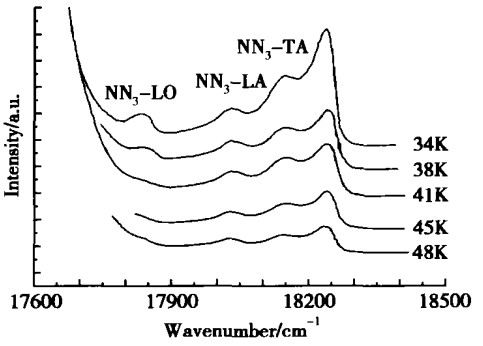

Fig. 4 Photoluminescence spectra of $GaP_{1-x}N_x$ (x = 0.12%) at 34～48K

For the case of $S^2\bar{n}(\bar{n}+1) \leq 1$, that is, at low temperature and week coupling, equation (1) can be simplified as

$$F_p \propto \frac{e^{-g} g^p}{p!} \tag{3}$$

where $g = S(\bar{n}+1)$, and thus the intensity ratio of one-phonon line to its zero-phonon line becomes

$$R = g = S(\bar{n}+1) \tag{4}$$

when $\bar{n} \ll 1$, $R \approx S$. In our experimental temperature $T < 50$K, for the LO phonon, $\bar{n}$ can be ignored ($\bar{n}_{LO^\Gamma} < 10^{-3}$), but for TA and LA phonons, $\bar{n}$ must be taken into accounted. We calculate the ratio of the integrated intensity of each NN_3 phonon sideband to the zero phonon line at different temperatures and obtained the S factors of NN_3 for TA, LA, and LO phonon sideband, as shown in Fig. 5. The results indicate clearly that the S factors are independent of temperature. This means the phonon sideband has the same temperature dependence as its zero phonon line. Our results provide a strong support to the conclusion made by Zheng[8]: that the coupling of nitrogen-bound exciton with its phonon in GaP∶N is consistent with the Huang-Rhys' multiphonon optical transition theory. Also, the simultaneous quenching of NN_i^* and NN_i (i = 4～7), despite these NN_i^* being lower than NN_3 in energy, disapproves the hypothesis that NN_i and NN_i^* are independent centers.

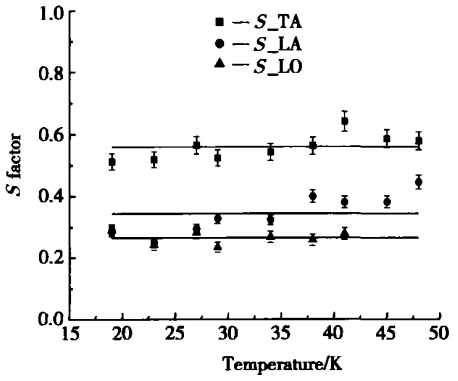

Fig. 5 Huang-Rhys' factors S derived from NN_3 of the sample $GaP_{1-x}N_x$ (x = 0.12%)

4 Conclusion

We show that in heavily N-doped GaP, due to the "concentration quenching" effect, the full NN_3 center spectrum (i.e., its zero phonon line and various phonon replicas) is revealed without the interference from the spectra of other higher energy centers (especially $NN_4 \sim NN_6$). Thus thermally quenching of GaPN at different temperatures from 19K to 48K have been studied. The various S factors we obtained are independent of temperature. This investigation offers a direct proof to that all the phonon replicas have the same temperature dependence with their correspondent zero-phonon line, which is consistent with the Huang-Rhys' multiphonon optical transition theory.

References

[1] Thomas D G, Hopfield J J, Froch C J. Isoeletronic traps due to nitrogen in gallium phosphide. Phys Rev Lett, 1965, 15: 857

[2] Allen J W. Isoelectronic impurities in semiconductors: a survey of binding mechanisms. J Phys C: Solid State Phys, 1971, 4: 1936

[3] Zheng J S, Yen W M. Luminescence decay of excitons bounds to nitrogen pairs in GaP: N. J Lumin, 1988, 39: 233

[4] Zhang Y, Ge W K. Behavior of nitrogen impurities in III-V semiconductors. J Lumin, 2000, 85: 247

[5] Huang K, Rhys A. Theory of light absorption and non-radiative transitions in F-centres. Proc Roy Soc, 1950, A204: 406

[6] Chang H, Hirlimann C, Kanehisa M, et al. Thermal quenching of bound exciton radiative recombination depending on the exciton phonon coupling in GaP: N and $GaAs_{1-x}P_x$: N. Sci Sin, 1982, A25: 942

[7] Zheng J, Zhang Y. Coupling of nitrogen-bound excitons with phonons in GaP: N. Sci Sin, 1986, A29: 862

[8] Zhang Y, Yu Q, Zheng J, et al. The phonon sidebands of NN_i pair emission in GaP: N. Solid State Commun, 1988, 68: 707

[9] Miyoshi S, Haguchi Y, Onabe K, et al. Metalorganic vapor phase epitaxy of $GaP_{1-x}N_x$ alloys on GaP. Appl Phys Lett, 1993, 63: 3506

[10] Baillargeon J N, Cheng K Y, Holfer G E, et al. Luminescence quenching and the formation of the $GaP_{1-x}N_x$ alloy in GaP with increasing nitrogen content. Appl Phys Lett, 1992, 60: 2540

[11] Bi W G, Tu C W. N incorporation in GaP and band gap bowing of GaN_xP_{1-x}. Appl Phys Lett, 1996, 69: 3710

[12] Zhang Y, Fluegel B, Mascarenhas A, et al. Optical transitions in the isoelectronically doped semiconductor GaP: N: An evolution from isolated centers, pairs, and clusters to an impurity band. Phys Rev, 2000, B62: 4493

[13] Wiesner P J, Street R A, Wolf H D. Exciton energy transfer in GaP: N. Phys Rev Lett, 1975, 35: 1366

重氮掺杂 GaP 中 NN_3 束缚激子与声子的耦合*

高玉琳[1]　吕毅军[1]　郑健生[1]　张　勇[2]　A. Mascarenhas[2]　辛火平[3]　杜武青[3]

(1 厦门大学物理系，厦门　361005)

(2 美国可再生能源实验室，戈尔登)

(3 美国加利福尼亚大学电机工程系，加利福尼亚)

摘要: 通过光致发光谱研究了在 19～48K 范围内掺氮浓度为 0.12% 时的 GaPN 的 NN_3 束缚激子与声子的耦合. 直接计算了 NN_3 束缚激子的 LO, TO 和 TA 声子伴线的黄昆因子 S, 除了 LO 声子外, 得到了 TO 和 TA 声子伴线的 S 因子在该温度范围内对温度的依赖关系. 计算表明, NN_3 的 LO, TO 和 TA 声子的 S 因子均与温度无关, 说明 NN_3 的 LO, TO 和 TA 声子伴线与它们的零声子线具有相同的温度依赖关系, 符合黄昆的多声子光跃迁理论.

关键词: GaPN; 光致发光; 等电子陷阱

PACC: 7280E; 7855E; 7865K

中图分类号: O472.3　　文献标识码: A　　文章编号: 0253-4177(2004)08-0889-05

* 国家自然科学基金(批准号: 60276002)和厦门大学预研基金(批准号: Y07005)资助项目

高玉琳　女, 1969 年出生, 博士, 主要从事 III-V 族半导体发光材料光学性质的研究.

2003-11-13 收到, 2004-02-10 定稿