Exciton-Phonon Coupling of NN₃ Center in Heavily Nitrogen Doped GaP*

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Abstract: Under heavy nitrogen doping, due to the "concentration quenching" effect, the full spectrum of the NN₃ 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.

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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 NN₁ exhibits a great similarity with that of the isolated center, except that NN₁ has an extra replica due to the nitrogen local mode. However, the comparison of any other nitrogen pair (NN$_i$ with $i \geqslant 3$) 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

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~ 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}~ 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× 10^{18}cm^{-3} under above gap excitation[6], where NN$_i^*$ represents the doublet feature associated with optical phonons (NN$_i$-LO$^\Gamma$ 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~ 18200cm^{-1} which composes of the phonon sidebands of NN$_4$~ NN$_7$ as well as NN$_3$. However, as shown in Fig. 2, when the nitrogen concentration reaches x = 0.12% (or [N] = 3.0×10^{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] = 3.0×10^{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

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

(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：

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

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

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

$$F_p \propto \frac{e^{-g}g^p}{p!} \qquad (3)$$

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

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

when $\bar{n} \ll 1$, $R \approx S$. In our experimental temperature $T < 50K$, 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 NN₃ phonon sideband to the zero phonon line at different temperatures and obtained the S factors of NN₃ 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 NN₃ in energy, disapproves the hypothesis that NN_i and NN_i^* are independent centers.
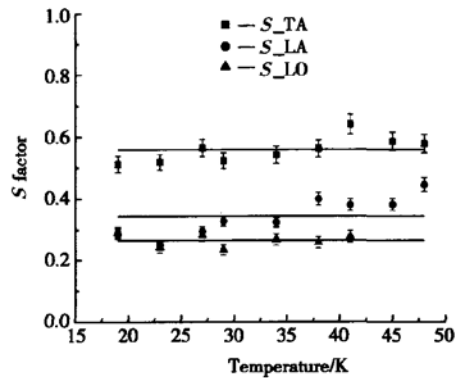
Fig. 5　Huang-Rhys'factors S derived from NN_3 of the sample $GaP_{1-x}N_x(x = 0.12\%)$

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.

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重氮掺杂 GaP 中 NN₃ 束缚激子与声子的耦合*

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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 NN₃ 束缚激子与声子的耦合. 直接计算了 NN₃ 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，NN₃ 的 LO, TO 和 TA 声子的 S 因子均与温度无关，说明 NN₃ 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

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