Radiative and nonradiative recombination of bound excitons in GaP:N. III. Reverse tunneling of bound excitons

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We investigate the features of the low-temperature luminescence spectra of GaP:N under the high-density selective excitation of excitons bound to NN_1 isoelectronic traps. The mechanism of the bound exciton tunneling from deep traps to shallow ones is discussed and the tunneling probability is derived. Luminescence dynamics analysis supports such a tunneling model.

I. INTRODUCTION

The bound-exciton tunneling effect in nitrogen-doped GaP and other III-V compound semiconductors has been studied for many years. Many features in low-temperature luminescence spectra have been well interpreted with this effect.[1] To our knowledge, all of these studies investigated the tunneling process from shallow nitrogen or nitrogen-pair traps to deep nitrogen-pair traps, which plays an important role in both excitation and decay processes, under band-gap excitation or selective excitation of shallow traps.

Measuring the low-temperature luminescence spectra of GaP:N under high-density selective excitation of the excitons bound to the deepest NN_1 traps, we observed a new luminescence phenomenon, which was interpreted as due to the bound exciton tunneling from deep traps to shallow ones.[2] This tunneling process obviously affects the luminescence spectrum under certain conditions. This result is supported by further study as we shall present below. Our present work contributes to the understanding of the dynamics of the excitons bound to isoelectronic traps and the interaction between crystal lattice and bound excitons.

In Sec. II, we present our experimental results. The tunneling mechanism and probability are discussed in Sec. III. Finally, we conclude in Sec. IV.

II. EXPERIMENT

At low temperature (10 K), under the high-density selective excitation of the excitons bound to NN_1 traps, we observed the luminescence of the excitons bound to shallower nitrogen traps as shown in Fig. 1. There appears in the spectrum the luminescence of the bound excitons with higher energy than that of laser photons of excitation, i.e., the luminescence of the excitons bound to NN_i ($i=3,4,5,6$) and isolated-nitrogen traps and of free excitons.

The samples used in our experiment are the liquid-phase epitaxial (LPE) GaP:N layer whose nitrogen concentration is $1\times10^{18}\text{cm}^{-3}$. The sample was mounted on a copper plate in a cryogenic system and the sample temperature can reach as low as 8 K. A dye laser pumped with pulsed neodymium-doped yttrium aluminum garnet (Nd:YAG) was used as the excitation source. The wave-number range of the dye laser is from 17 650 to 18 030 cm^{-1}. Focused, the dye laser can easily reach the power density as high as 3×10^7 W/cm^2. With the Spex Industries double grating monochromator and boxcar averager, the luminescence spectra were plotted and recorded by a microcomputer.

To investigate the excitation mechanism of the excitons bound to NN_i($i=3,4,5,6$) and isolated-nitrogen traps under the condition of the selective excitation of the excitons bound to NN_1 traps, we carried out the experiment measuring the excitation spectrum of NN_3 excitons which gave the strongest luminescence except NN_1 excitons. At 9 K, monitoring the luminescence of NN_3 excitons, the excitation spectrum was produced by scanning the excitation laser from 18 030 to 17 650 cm^{-1}, as shown in Fig. 2. Although we cannot see the contribution of the direct absorption of NN_1 excitons to the luminescence of NN_3 excitons in this experiment because the wave number of our dye laser cannot reach the range of the direct absorption of NN_1, which is around 17 610 cm^{-1}, the spectrum is important to our interest. The excitation peak at 18 012 cm^{-1} and the energy of NN_1 exciton plus an intrinsic LO phonon of GaP crystal (17 610+402 cm^{-1}) coincide exactly. This means that the excitation of NN_3 excitons originates from that of NN_1 excitons and the interaction between the bound ex-

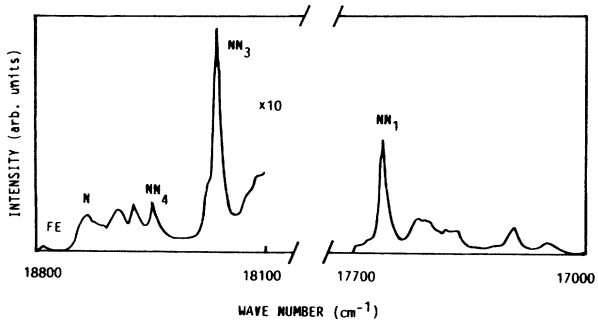

FIG. 1. Luminescence spectrum of GaP:N. Excitation wave number is 17 850 cm^{-1}. Excitation density if 2×10^7 W/cm^2. Temperature is 10 K.

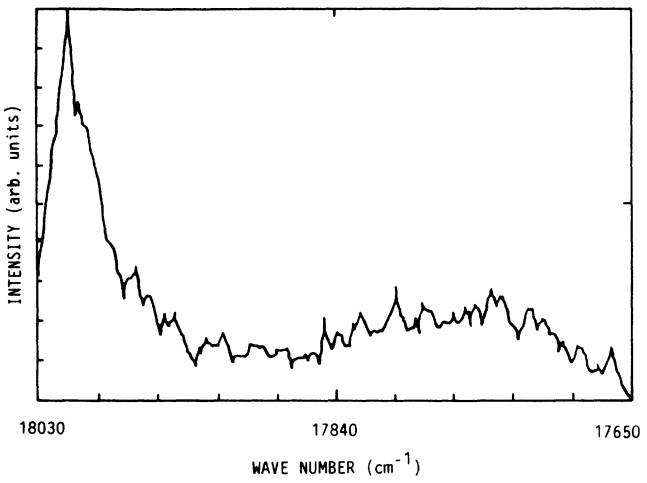

FIG. 2. Excitation spectrum of the luminescence of NN_3 excitons. Temperature is 10 K.

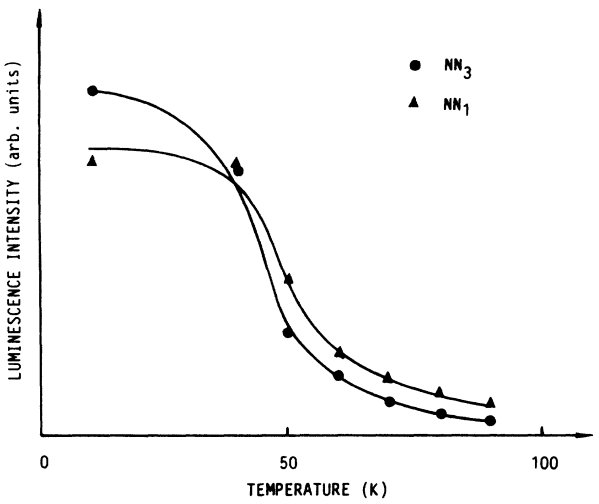

FIG. 4. Temperature behavior of the luminescence of NN_1 and NN_3 excitons.

citons and the crystal lattice. As we will discuss in Sec. III, it is the direct evidence that the tunneling of the bound excitons from deep traps to shallow ones may occur under certain conditions.

Figure 3 shows the luminescence decay curves of NN_1 excitons and NN_3 excitons. The temporal width of the excitation pulse is 7 ns and the repetition rate is 15 Hz. Fitted with the formula derived in the next section, the experimental results support the tunneling mechanism model, which will be depicted in detail in the next section.

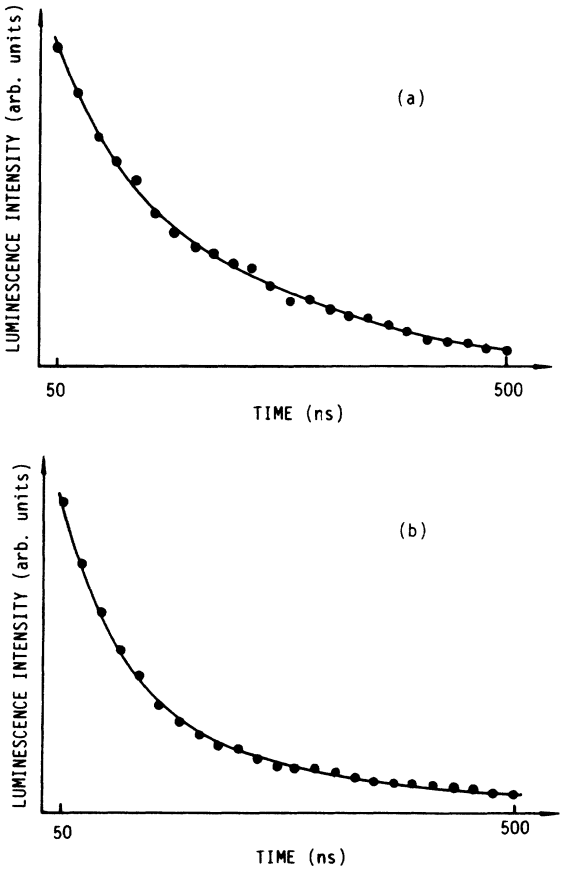

FIG. 3. Decay curves of the luminescence of (a) NN_1 and (b) NN_3. Dots are experimental results, lines are results from dynamics analysis.

We also determined the temperature dependence of the luminescence of NN_1 and NN_3 excitons in our experiment. Figure 4 shows the luminescence intensity sample temperature relations. These relations are the same as that under normal band-gap excitation conditions. As we will see below, these results are reasonable.

III. DISCUSSION

There are several possible ways in which bound excitons may decay.[3] They include radiative transition with or without phonon emission, nonradiative transition by multiphonon emission, nonradiative transition by the Auger effect, tunneling of a bound exciton to another impurity center with or without phonon assistance, tunneling of the hole of a bound exciton to an ionized acceptor of neutral donor, thermal emission of the hole, of the bound exciton as a single entity or of both the hole and electron as free particles, etc.

Since the Auger effect requires a nearly third particle to which the energy of the bound exciton transfers, and since in pure samples such a third particle is not present, the nonradiative transition by the Auger effect is inoperative. To the excitons bound to nitrogen traps, the binding energy between the isoelectronic trap and the bound electron is much smaller than that between the bound electron-trap complex and the hole of a bound exciton [for the isolated nitrogen trap, the former is only 0.6 meV and the whole binding energy is about 20 meV (Ref. 4)], so the tunneling of the whole exciton to another center is more favorable than that of the hole to another center. At low temperature, the thermal emission of the hole, the whole exciton, or both the hole and electron as free particles is also inoperative. Thus, the decay mechanism of

the excitons bound to nitrogen traps consists of the radiative transition with or without phonon emission, the nonradiative transition by multiphonon emission, and the tunneling of the whole bound exciton to another nitrogen trap with or without phonon assistance.

Under our selective excitation condition, only NN_1 excitons are originally excited by laser. After excitation, the NN_1 excitons decay in the above three ways. On the other hand, the other nitrogen traps which have a smaller binding energy cannot be excited by laser or by reabsorbing the emission light of NN_1 excitons. The excitation mechanism of nitrogen traps other than NN_1 traps is the tunneling of the whole exciton from NN_1 trap with phonon assistance, as the excitation spectrum of the luminescence of NN_3 excitons shows in Sec. II. The existence of the mechanism of bound-exciton tunneling with phonon assistance which allows excitons to migrate down to lower-energy traps has been demonstrated by time-resolved experiment.[5] Such a transfer is reasonable for the fact that the nitrogen pairs that dominate the emission under normal band-gap excitation condition account for less than 1% of the total nitrogen content.

In insulated materials, the tunneling effect caused by dipole-dipole interaction is usually responsible for energy transfer. The tunneling occurs over a distance of about 10 Å.[6] But in the GaP:N, the average distance between a nitrogen trap and its nearest-neighbor nitrogen trap is much larger than this value. Assuming a random distribution of nitrogen atoms and continuum approximation, for our sample, the concentration of NN_1 is about 4×10^{14} cm^{-3} and the probability that a NN_1 trap has a nearest isolated nitrogen trap over the distance of 54 Å is the largest. Due to the very large spatial extent of the wave function of the excitons bound to isoelectronic traps, the exciton tunneling in GaP:N may occur over a considerably large distance.[1] Since isoelectronic traps are partly formed by the distortion of the GaP crystal lattice, the excitons bound to these traps have a strong interaction with the host lattice. The tunneling from deep traps to shallow ones accompanied by the absorption of phonons is reasonable. If the excitation is sufficiently strong, this process should be observable in the luminescence spectrum. Because the average distance between a NN_1 trap and another nitrogen-pair trap is about 2 orders of magnitude larger than that between a NN_1 trap and an isolated nitrogen trap, only the tunneling from NN_1 traps to isolated nitrogen traps is of importance.

The probability of the tunneling from NN_1 traps to N traps can be expressed as[7]

$$P(R)=P_0\exp(-2R/a)\ , \tag{1}$$

where R is the distance between the center of the NN_1 trap and the nearest isolated nitrogen trap, a is the effective exciton radius, which is a combination of the radii of NN_1 exciton and N exciton, constant P_0 is typically about 10^{11} sec^{-1} for the tunneling from shallow traps to deep ones, while a is taken 32 Å.[5]

To compare with experimental results and to obtain tunneling probability, we consider the dynamic processes. Being relatively weak, the luminescence of the excitons bound to all nitrogen traps other than isolated nitrogen, NN_1 and NN_3 traps are eliminated. Thus, we have a rather simple dynamic model as shown in Fig. 5.

Although we used the high-excitation-density laser to excite samples, there is no plasma or other high-density carrier phase produced because of the small absorption coefficient. The high-excitation-density laser is used only to create sufficiently large number of NN_1 excitons to make the tunneling process from NN_1 traps to N traps observable in the luminescence spectrum.

Because of the high excitation density, it can be assumed that the NN_1 level has been excited to a steady state whenever the excitation pulse starts. During the period that the excitation pulse lasts, the generation rate of NN_1 excitons G is always the same as the decay rate of NN_1 excitons. To the N level, there exist two processes: tunneling from the NN_1 level and radiative and nonradiative (include tunneling to all other nitrogen trap levels) transitions. The same is true for the NN_3 level as shown here:

$$\begin{aligned} 0&=G-\frac{n_1}{\tau_1}\ ,\\ \frac{dn_3}{dt}&=-\frac{n_3}{\tau_3}+P_3'n_\infty\ ,\\ \frac{dn_\infty}{dt}&=-\frac{n_\infty}{\tau_\infty}+p_1n_1\ , \end{aligned} \tag{2}$$

where n_1, n_3, and n_∞ are the number of excitons bound to NN_1, NN_3, and N traps, respectively. τ_1, τ_3, and τ_∞ are the luminescence lifetime of NN_1, NN_3, and N traps, respectively. P_1 is the probability of tunneling from NN_1 traps to N traps, and P_3' is that of the tunneling from N to NN_3 traps. After an excitation pulse ends, the dynamic processes of NN_1, NN_3, and N levels can be described as follows:

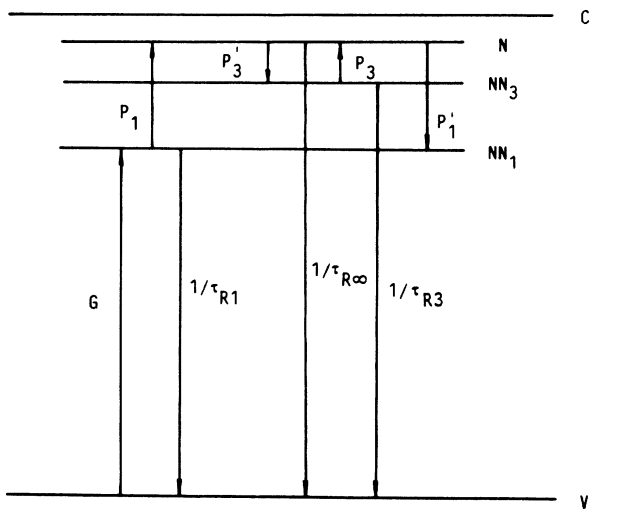

FIG. 5. Dynamic model of GaP:N under selective excitation of NN_1 level. Nitrogen trap levels other than N, NN_1, and NN_3 are excluded due to their relatively weak luminescence.

$$\frac{dn_1}{dt} = -\frac{n_1}{\tau_1} + p_1' n_\infty ,$$
$$\frac{dn_3}{dt} = -\frac{n_3}{\tau_3} + p_3' n_\infty , \quad (3)$$
$$\frac{dn_\infty}{dt} = -\frac{n_\infty}{\tau_\infty} ,$$

where P_1' is the probability of the tunneling from the N to NN_1 level. All the P_i' ($i=1,2,3,\ldots$) is simply included in $1/\tau_\infty$.

From Eq. (2), we get the numbers of NN_1, NN_3, and N excitons at the moment that an excitation pulse ends. These are used as the initial conditions for solving Eq. (3). In this way, the luminescence decay curves are derived. Fitting these curves with experimental results as shown in Fig. 3, we get $\tau_1=120$ ns, $\tau_3=105$ ns, $\tau_\infty=400$ ns, and $P_0=5.9\times10^7$ sec^{-1}. The values of these lifetimes are consistent with the earlier work.[8] P_0 is about 3 orders of magnitude smaller than that for the tunneling from shallow traps to deep ones, but it is much larger than the total probability of the radiative and nonradiative processes of the NN_1 level. So the tunneling process can be observed in the luminescence experiment only if the excitation has a sufficiently high density and the lasting period of the excitation pulse is long enough in addition to the high nitrogen concentration. Under the condition of the band-gap excitation or selective excitation of shallower traps, it is because the tunneling from shallow to deep traps overwhelms the reverse tunneling process that the reverse tunneling process does not cause noticeable change in luminescence spectra.

In Eq. (3), we notice that the decay processes are the same as that under the condition of band-gap excitation or selective excitation of isolated-nitrogen traps. This result is supported by experiment. Figure 4 shows the temperature-dependence relations of the luminescence of NN_1 and NN_3 excitons under the selective excitation of NN_1 excitons. These results are not very accurate because of the weak luminescence at higher temperatures, but they show the tendency clearly.

IV. CONCLUSION

In GaP:N, the tunneling of bound excitons from shallow nitrogen traps to deep ones plays an important role in the excitation transfer. We show that there also exists the reverse tunneling process from deep traps to shallow ones. As this reverse process is much weaker than the former process, only the tunneling from shallow traps to deep ones is observable and the reverse process can be omitted under the condition of the normal band-gap excitation or selective excitation of shallow traps. Under the high-density selective excitation of deeper traps, this reverse process plays an important role in the excitation transfer and becomes observable in the luminescence spectrum. Taking this into account, the dynamics analysis satisfies experimental results well.

In short, there exist the tunneling processes both from shallow to deep nitrogen traps and from deep to shallow ones. Although the probability of the latter process is much smaller than that of the former one, the tunneling from deep nitrogen traps to shallow ones is still observable under certain conditions.

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[1]P. J. Wiesner, R. A. Street, and H. D. Wolf, Phys. Rev. Lett. **35**, 1366 (1975); J. A. Kash, Phys. Rev. B **29**, 7069 (1984).
[2]Q. Hong, K. Dou, and X. Y. Zhang, J. Lumin. **40&41**, 525 (1988).
[3]M. D. Sturge, E. Cohen, and K. F. Rodgers, Phys. Rev. B **15**, 3169 (1977).
[4]W. T. Masselink and Yia-Chung Chang, Phys. Rev. Lett. **51**, 509 (1983).
[5]P. Leroux-Hugon and H. Mariette, Phys. Rev. B **30**, 1622 (1984).
[6]B. Di Bartolo, *Optical Interactions in Solids* (Wiley, New York, 1968), Chap. 18.
[7]A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1968).
[8]J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 763 (1967); J. A. Kash, J. H. Collet, D. J. Wolford, and J. Thompson, Phys. Rev. B **27**, 2294 (1983).