

Lifetime study of N impurity states in GaAs_{1-x}N_x (x=0.1%) under hydrostatic pressure

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The lifetimes of a series of N-related photoluminescence lines (A₂–A₆) in GaAs_{1-x}N_x (x=0.1%) were studied under hydrostatic pressures at ~30 K. The lifetimes of A₅ and A₆ were found to increase rapidly with increasing pressure: from 2.1 ns at 0 GPa to more than 20 ns at 0.92 GPa for A₅ and from 3.2 ns at 0.63 GPa to 10.8 ns at 0.92 GPa for A₆. The lifetime is found to be closely correlated with the binding energy of the N impurity states, which is shown either in the pressure dependence for a given emission line or in the lifetime variation from A₂ to A₆. © 2006 American Institute of Physics. [DOI: 10.1063/1.2205729]

Nitrogen doped III-V semiconductors GaP and GaAs have been investigated extensively for several decades. Especially in recent years heavily N doped GaAs_{1-x}N_x alloy has been given more attention because of its potential in optoelectronic applications and unusual physical properties. In sufficiently heavily doped GaAs:N samples, a series of N-related below-band-gap transitions have been observed.¹⁻⁴ However, the origins of these levels, either associated with different N pairs or N clusters, remain controversial.

The dynamics process of a radiative recombination center can be acquired by the time-resolved photoluminescence measurement, and it allows us to further explore the electronic structure in GaAsN. Pressure experiment has been extensively used to study GaAsN alloys. Application of pressure can change the relative energy position between N-related levels and the host conduction band edge or tune the resonant N impurity states lying above the conduction band edge into the forbidden gap, and thus make them radiative. However, no time-resolved photoluminescence measurements under hydrostatic pressure for GaAsN alloy were performed yet. It is expected that a deeper insight to the N induced electronic states can be obtained by combining the pressure and lifetime measurement. In this work, we perform time-resolved photoluminescence (PL) measurements under hydrostatic pressure at 30 K for the set of N-related PL lines, A₂–A₆, previously observed for a GaAs_{1-x}N_x sample with x=0.1%.¹ We observe a correlation between the photoluminescence lifetime and the impurity binding energy that either can be tuned by applying pressure for a given N impurity center or varies from one N impurity center to the other.

The GaAs_{1-x}N_x sample investigated here was grown by gas-source molecular beam epitaxy on a semi-insulating (001) GaAs substrate. The epilayer thickness is nominally 400 nm. The nitrogen concentration was determined by the high-resolution x-ray rocking curve measurement and theo-

retical dynamical simulation to be 0.10%. The detailed growth process has been described elsewhere.⁴

For the hydrostatic pressure experiments the sample was loaded in a diamond-anvil cell (DAC) used to generate pressures up to 1.55 GPa. Condensed argon was used as the pressure-transmission medium. The pressure was determined from the shift of the ruby R₁ fluorescence line. The PL spectra and the lifetimes were measured at low temperature with the DAC mounted in a He closed-cycle cryogenic refrigeration system.

The PL spectra were measured by a Jobin-Yvon T64000 micro-Raman system with a cooled multichannel charge coupled device (CCD). The excitation source is the 514.5 nm line of an Ar⁺ laser. The power was about 0.5 mW and the spot size on the sample is around 30 μm. For the time-resolved PL, the Ti:sapphire mode-locked laser was used as an excitation light source and the time-correlated signal was analyzed by a two dimensional (2D) synchroscan streak camera with an overall resolution of better than 20 ps.

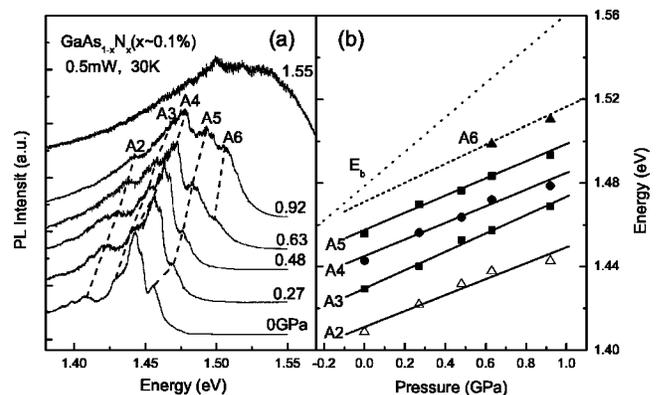


FIG. 1. (a) The PL spectra at different pressures and N-related bound exciton emission peaks denoted as A₂–A₆. (b) The corresponding pressure dependences of the PL peak positions. The solid lines are the linear fits to the experimental data. The pressure dependence of A₆ (the dash line) and alloy band gap E_b (the dotted line) are taken from Ref. 1.

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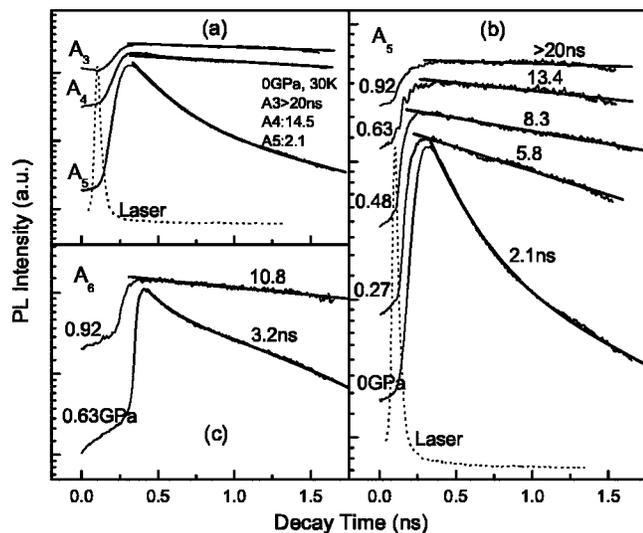


FIG. 2. (a) Decay curves of $\text{GaAs}_{1-x}\text{N}_x$ for A_3 – A_5 at 30 K under ambient pressure. The inset lists the corresponding lifetimes. (b) Decay curves of A_5 and (c) A_6 under different pressures at 30 K. Their pressures and lifetimes are denoted on the left and right of the decay curves, respectively.

Figure 1(a) shows the PL spectra of the $\text{GaAs}_{1-x}\text{N}_x$ sample ($x \sim 0.1\%$) under 514.5 nm cw excitation with a power of about 0.5 mW at different pressures. These spectra are nearly the same as those have been obtained previously.^{1,5} Four peaks were observed at 1.409 (A_2), 1.429 (A_3), 1.443 (A_4), and 1.456 eV (A_5), respectively. Similar peaks have previously been reported and assigned to different nitrogen pairs, N clusters, or their optical phonon replicas, although the spectral shape and relative intensity of the peaks may vary in different works. For example, A_5 is attributed to a N pair (NN_E) in Refs. 5 and 6, unknown origin (X_4) in Ref. 7, and the LO-phonon replica of N-cluster states.⁸ Ma *et al.*¹ have concluded that these transitions are the zero-phonon lines from different nitrogen-cluster centers by carefully investigating their temperature and pressure dependence. The band gap of this sample was determined to be $E_b = 1.478$ eV by Luo *et al.* under the condition of short pulse excitation at 14 K.⁵ As is plotted in Fig. 1(a), all the peaks blueshift with increasing pressure. When the pressure reaches 0.63 GPa, a peak appears at 1.499 eV (labeled as A_6), which also blueshifts under pressure. As around 1.55 GPa, these peaks start to merge into a broadband and become less distinguishable. The broadening of the PL peaks is due to the strengthened interaction among different nitrogen impurities.

Figure 1(b) depicts the dependences of the peak positions on pressure. The solid lines are the results of fitting experimental data using equation $E(P) = E_0 + \beta P$, where P is the pressure and β is the pressure coefficient. The pressure coefficients β_i ($i=2-5$) for A_2 – A_5 are all found to be near 40 meV/GPa: 38(5), 44(2), 40(5), and 41(4) meV/GPa, respectively, which agree with the results of Ma *et al.*¹ and is also comparable to that reported in an earlier work.³ For A_6 , since we only obtain two data points, the line shown in the figure is taken from the fitting of Ref. 1, which, in fact, shows a good agreement between the two studies. Also shown in Fig. 1(b) is the pressure dependence of alloy band edge E_b taken from Ref. 1. It is found that when the pressure dependence of A_6 is extrapolated to 0 GPa, its peak energy is 1.471 eV, which is just below but close to the band energy of

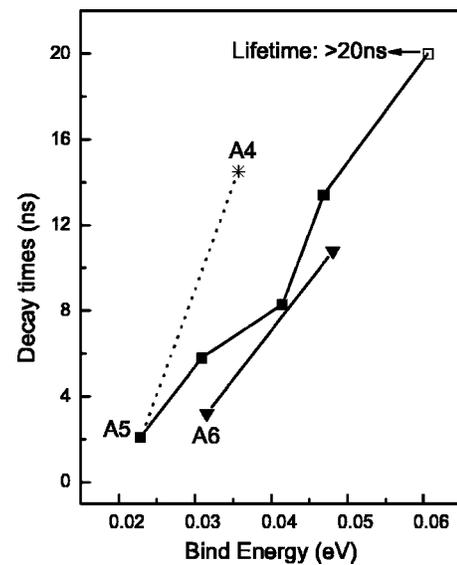


FIG. 3. The lifetime vs. the binding energy for A_5 and A_6 . The lifetimes of A_4 and A_5 at 0 GPa are connected by the dot line. The open square denotes the lifetime of A_5 at 0.92 GPa (> 20 ns).

E_b (1.479 eV) at 0 GPa. Zhang *et al.*⁹ have studied the evolutions of two N-related emissions X_1 and X_2 with N concentration in the range of 10^{15} – 10^{19} cm^{-3} . They become nearly resonant with E_{gx} , a hostlike band edge excitonic absorption peak, at $[\text{N}] \sim 10^{19}$ cm^{-3} . In our case, the proximity of A_6 and E_b seems to suggest that A_6 could be related to NN_1 or NN_2 (X_1 or X_2).

Figure 2 shows the PL decay process for various N-related exciton emissions and/or under different hydrostatic pressure. In the measurement, the PL decay curves were monitored at the respective PL peak energies. As it is well known that at low temperatures, the decay of N bound exciton is typically dominated by the radiative recombination, if the carrier transfer to the lower energy states are negligible.¹⁰ Note that most decay curves can be approximately described by a single exponential function, although the decay curves for higher energy peaks, such as A_5 at 0 GPa and A_6 at 0.63 GPa are not single exponentials. For these cases, the decay curves are fitted with double exponential functions. The obtained decay times of the two processes are 0.26 and 2.1 ns for A_5 at 0 GPa and 0.15 and 3.2 ns for A_6 at 0.63 GPa. The initial rapid decrease could be due to the carrier transfer to the lower levels, therefore we attribute the slower component to the radiative lifetime. In the figure we just denote the decay time for the slower decay process. The solid straight lines are the fitted results. Figure 2(a) shows the decay curves of A_3 , A_4 , and A_5 at 0 GPa. Their lifetimes, listed in the inset, are 2.1 ns for A_5 , 14.5 ns for A_4 , and > 20 ns for A_3 (instrument limited), comparable to the results reported by Luo *et al.*:⁵ 3 ns for A_5 (NN_E) and 8 ns for A_4 (NN_D) at 14 K. The decay curves for A_5 and A_6 at different pressures are plotted in Figs. 2(b) and 2(c). The decay times of A_3 and A_4 under the pressures are longer than the detection limit of the system. We can easily see that the higher is the pressure the longer is the lifetime.

We notice that at ambient pressure from A_5 to A_2 , the PL lifetime increases in the order of increasing the binding energy of the N impurity center. There are two possible explanations for this observation. One is that a N impurity center with a larger binding energy intrinsically has a longer radiative

TABLE I. The binding energies ΔE_i ($i=4-6$) and the corresponding PL decay times τ_i at different pressures.

Pressure (GPa)	A_4		A_5		A_6	
	ΔE_4 (meV)	τ_4 (ns)	ΔE_5 (meV)	τ_5 (ns)	ΔE_6 (meV)	τ_6 (ns)
0	36	14.5	23	2.1		
0.27			31	5.8		
0.48			41	8.3		
0.63			47	13.4	32	3.2
0.92			61	>20	48	10.8

tive decay time, because its wave function is expected to be composed of more k components away from the Γ point. The other one is that a higher energy state is more affected by the carrier relaxation or energy transfer to states of lower energies, thus has a shorter PL decay time that is not just determined by the radiative decay.¹⁰⁻¹²

Figure 3 shows the dependence of the lifetime on the binding energy of the impurity center, here the binding energy is defined as $\Delta E_i(p) = E_b(p) - E_i(p)$ ($i=4-6$), E_i is the energy position of A_i , and E_b is the alloy band edge. The obtained binding energies are listed in Table I, along with the corresponding PL decay times. The solid lines in Fig. 3 connect the data of each PL peak at different pressure, and the dot line links the lifetimes for different PL peaks measured at atmospheric pressure. It can be seen from Fig. 3 and Table I that when the binding energy increases from 23 to 36 meV (from peak A_5 to A_4) at ambient pressure, the lifetime increases from 2.1 to 14.5 ns. However, the lifetime of A_5 only increases from 2.1 to 8.3 ns when its binding energy increases from 23 to 41 meV by applying pressure. Thus, the increase of lifetime from one peak to another deeper peak at atmospheric pressure results from both the increase of the binding energy and the weakening of the energy transfer effect. The smaller increase of the lifetime with pressure for A_5 implies that the increase of the binding energy dominates the change of lifetime with increasing pressure. The effect of energy transfer process is not expected to be the dominant cause for the increase of lifetime with pressure since the relative energy positions of the different N-related levels do not change with the applying pressure and there are no drastic changes in the relative intensities among A_i ($i=2-5$) PL peaks.

It is interesting to compare GaAs:N with GaP:N. In the case of indirect band gap GaP:N, the localized N impurity potential introduces a small amount of the Γ component in the wave function of the N bound state, which leads to a shortened radiative decay time compared to that of a shallow donor bound exciton.¹³ Also, it has been found that in a P-rich GaP_{1-x}As_x:N, pressure reduces the binding energy of the N bound exciton, which thus enhances the energy transfer from a shallower N bound state to a deep one.¹⁴ In the case of GaAs:N, however, the radiative decay time for a N bound exciton seems to be significantly longer than that of a shallow donor bound exciton, ~ 1 ns.¹⁵ And the energy transfer may be suppressed by applying pressure, especially for those N bound states near the conduction band edge. The appearance of A_6 under pressure clearly indicates the significance of the transfer process that is partially suppressed by the increase of binding energy due to the pressure. Such

comparison shows that the highly localized isoelectronic impurity potential may manifest itself in very different or almost opposite ways in different hosts.

In summary we have studied the low temperature PL spectra of GaAs_{1-x}N_x ($x=0.1\%$) and the lifetimes of its different PL peaks in the pressure range of 0–1.55 GPa. Four N-related PL peaks below the alloy band edge were observed at atmospheric pressure. Their energy positions are 1.409 (A_2), 1.429 (A_3), 1.443 (A_4), and 1.456 eV (A_5), respectively. The lifetime of A_5 and A_4 is 2.1 and 14.5 ns at 30 K under atmospheric pressure. These peaks shift to high energy altogether with a rate of about 40 meV/GPa according to the increase of the pressure. A peak A_6 appears while the pressure is beyond 0.63 GPa. The lifetimes for A_5 and A_6 increase rapidly with the increase of the pressure. Our results and analyses reveal a correlation between the radiative lifetime and the binding energy for a N induced bound state, which can be understood in terms of one intrinsic reason, the strength of the binding potential, and the other extrinsic reason, the energy relaxation.

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