# Evidence for Radiative Recombination in $GaAs_{1-x}P_x$:N ($0.28 \lesssim x \lesssim 0.45$) Involving an Isolated Nitrogen Impurity State Associated with the $\Gamma_1$ Minimum*

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(Received 8 March 1976)

Photoluminescence data for $GaAs_{1-x}P_x$ alloys implanted with nitrogen are reported for $0.28 \lesssim x \lesssim 1.0$ and for N concentrations from $10^{16} \lesssim N_N \lesssim 10^{20}$ cm$^{-3}$. Evidence is presented of a new excited shallow bound state ($N_\Gamma$) of the isolated N impurity, coexisting with the tightly bound ground state ($N_X$) of this center. The two levels are associated primarily with nonequivalent conduction-band minima.

Isolated nitrogen impurities in GaP and $GaAs_{1-x}P_x$ produce an electronic level associated with the $X_1$ conduction-band minima. Luminescence from radiative decay of excitons bound to this level is termed $A$-line emission[1] in GaP and recently $N_X$ emission in $GaAs_{1-x}P_x$.[2-4] Previously, there was believed to be only one level produced by the isolated impurity in $GaAs_{1-x}P_x$.[5-11] In this paper, however, we present evidence of a second bound level and its emission line $N_\Gamma$. This new level, unlike $N_X$, is associated with the $\Gamma_1$ minimum and is observable over only a limited range of ternary alloy compositions ($0.28 \lesssim x \lesssim 0.45$).

Data presented here are obtained from extensive photoluminescence (PL) studies of N-implanted $GaAs_{1-x}P_x$ over the alloy composition range $0.28 \lesssim x \leq 1.0$, and over a wide range of N concentrations ($10^{16} \lesssim N_N \lesssim 10^{20}$ cm$^{-3}$). Recent progress in the annealing of N-implanted GaP[3] and $GaAs_{1-x}P_x$,[2,3,12-14] resulting in material quality comparable with that of conventionally doped crystals, has made this study possible. The PL measurements are performed at 4.2 K on vapor-phase exitaxial $n$-type crystals of bulk dimensions having low donor concentration ($N_D < 10^{17}$ cm$^{-3}$). Spectral changes due to the N doping are clearly identifiable and are easily distinguished from radiation damage[12-14] and other doping effects. A portion of the N-implanted region on each sample is removed for direct comparison with N-free material. Discussion of sample implantation, passivation and annealing, and PL measurements are presented elsewhere.[2,3,12-14] The N concentrations referred to below are theoretical peak concentrations for single $^{14}N^+$ implantations at 200 keV.[12]

Photoluminescence spectra from $GaAs_{1-x}P_x$ ($x = 0.34$) are shown in Fig. 1. The bottom spectrum, labeled $\Gamma$ (composed of free exciton, band-to-band, and shallow donor-related emission), is from annealed N-free material. With addition of the N impurity to $N_N \sim 5\times10^{16}$ cm$^{-3}$, the $N_\Gamma$ and $N_X$ transitions are observed. Appearance of $N_X$ at this low concentration agrees with studies in all N-implanted $GaAs_{1-x}P_x$ ($x \gtrsim 0.28$), where $N_X$ is systematically observed for $N_N \sim 10^{16}$ cm$^{-3}$. At this N concentration, $A$-line emission is observed in GaP, but NN-pair emission is absent.[1,3] As indicated by the scale multipliers, the $N_\Gamma$ intensity grows with N concentration and then decreases for $N_N \gtrsim 5\times10^{17}$ cm$^{-3}$, while $N_X$ intensity increases and dominates the spectrum for $N_N \gtrsim 5\times10^{18}$ cm$^{-3}$. For the excitation power density used here ($2.5\times10^3$ W cm$^{-2}$ at 4880 Å) the $N_\Gamma$ transition is difficult to observe for high N doping.

The crystal-composition dependences of the $N_\Gamma$ and $N_X$ states in N-implanted material are displayed in Fig. 2. The $\Gamma_1$ and $X_1$ band-edge dependences follow those given by Onton and Foster[15] at 6 K. Each N luminescence data point represents many individual observations at each indicated alloy composition for $10^{16} \lesssim N_N \lesssim 10^{20}$ cm$^{-3}$. Emission from $N_\Gamma$ follows the $\Gamma_1$ band edge over

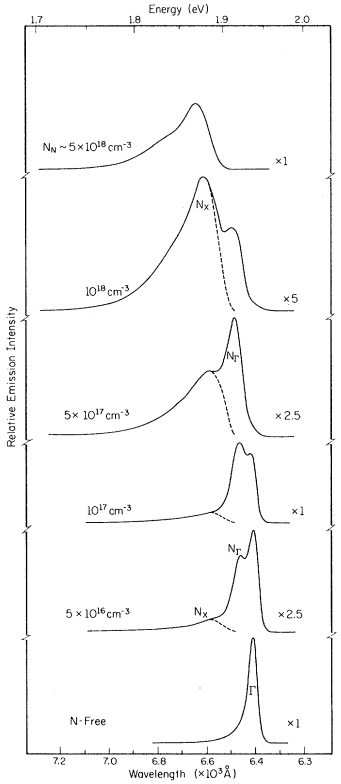


FIG. 1. Photoluminescence spectra (4.2 K) of $GaAs_{1-x}P_x$ ($x=0.34$) N-implanted to the indicated peak concentration and annealed for 30 min at 950°C. Dashed portions of the spectra approximate the $N_X$ band shape.

a wide composition range ($0.28 \lesssim x \lesssim 0.43$) with $E_\Gamma - E_{N_\Gamma} = 19 \pm 2$ meV. For $x \gtrsim 0.43$ the $N_\Gamma$ state departs from $\Gamma_1$ and evolves into the state labeled $N_{\Gamma-X}$. This level follows approximately the $X_1$ dependence from $x \gtrsim 0.46$ to its disappearance at $x \gtrsim 0.53$.

Luminescence peaks corresponding to $N_\Gamma$ (or $N_{\Gamma-X}$) have been variously reported in the spectra of $GaAs_{1-x}P_x$ N-doped to low concentrations during growth.[7-10] However, in the absence of N concentration variability now provided by ion implantation, the interpretation of these spectra was unclear. For $x \gtrsim 0.40$, $N_\Gamma$ or $N_{\Gamma-X}$ emission was attributed to $A$-line recombination[8-10] at the isolated N center, associated with the $X_1$ conduction-band minima as in GaP. This was believed to be the only bound state of the isolated center and was assumed to become degenerate with the $\Gamma_1$ continuum for $x \gtrsim 0.40$.[8-11] In $x = 0.37$ material $N_\Gamma$ was reported as $NN_3$-pair emission,[16] in analogy with GaP.[1] The remaining emission bands associated with $N_X$ were attributed to NN-pair recombination.[8-10,16] Recent implantation studies reveal no evidence of NN-pair participation for

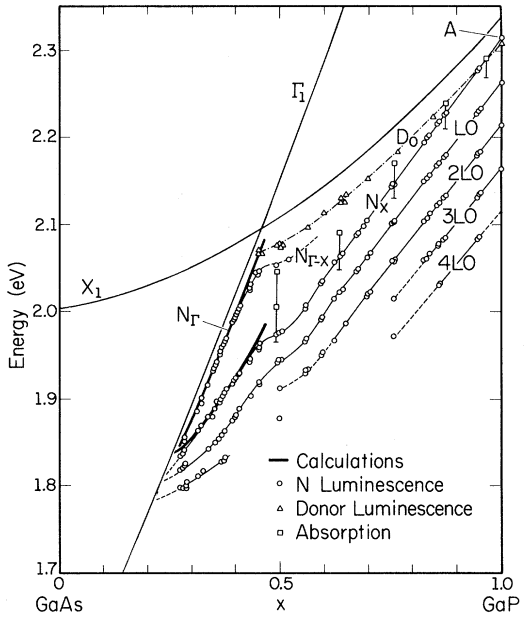


FIG. 2. $GaAs_{1-x}P_x$: N alloy composition diagram (4.2 K) resulting from N-implantation data.

$x \lesssim 0.90$ in $GaAs_{1-x}P_x$.[3] The $N_x$ emission peak for $0.28 \lesssim x < 1.0$ is due to bound-exciton recombination at the ground state of the isolated N center associated with the $X_1$ conduction-band minima.[2-4] Major peaks below $N_X$ result from optical phonon sidebands of this no-phonon transition.[3]

The present data suggest that $N_\Gamma$ (and $N_{\Gamma-X}$) emission also results from bound-exciton recombination at the isolated center. However, the level $N_\Gamma$ appears as a shallow excited state of the impurity, associated instead with the $\Gamma_1$ minimum. Moreover, evolution of $N_\Gamma$ into the $N_{\Gamma-X}$ state results from hybridization of the level as $N_\Gamma$ approaches $X_1$. In the PL spectra this appears as a broadening and deepening of the level compared to $N_\Gamma$ of Fig. 1.

Although the focus of the present discussion is the new $N_\Gamma$ state, the remaining data appearing in Fig. 2 are presented for completeness. Donor emission ($D_0$) due to the background S, Se, or Te dopant is shown for indirect-band-gap compositions. Data from optical absorption measurements on N-doped $GaAs_{1-x}P_x$ are also presented in Fig. 2, where the square symbols represent approximate absorption peak positions and the horizontal bars indicate the onset of the N-induced absorption. Compared to the $N_X$-related emission peaks, the absorption data are indicative of a center strongly coupled to the lattice, with a resultant Stokes shift in absorption.[3,4,17,18]

The additional high-energy absorption peak at $x = 0.49$ apparently results from direct absorption on the $N_{\Gamma-X}$ level, observable weakly in emission at this composition.

An oversimplified but analytic description of the $N_\Gamma$ and $N_X$ levels is afforded by neglecting the electron-hole (~5–10 meV) and electron-electron interactions, assuming the hole is free, and describing the electron-N interaction by a local potential $V(r) = -V_0 \operatorname{sech}^2(r/a)$. The electron band structure is assumed to be isotropic and parabolic, near both $\Gamma_1$ and $X_1$, with effective masses $m_\Gamma = 0.063 + 0.052x$ [19] and $m_X = 0.35 + 0.015x$.[20] Coupling among the three $X_1$ minima and valley-orbit splitting are neglected. Then, the binding energies of electrons in the states $N_\Gamma$ and $N_X$ are (with $\nu = \Gamma$ or $X$)

$$R_\nu = \frac{\hbar^2}{8m_\nu a^2}\left[\left(1+\frac{8m_\nu V_0 a^2}{\hbar^2}\right)^{1/2} - 3\right]^2. \quad (1)$$

Here we have assumed that the effective-mass approximation is valid separately at the $\Gamma_1$ and $X_1$ minima; we have used a formalism due to Bassani,[21] and we have neglected intervalley coupling. The quantities $V_0(x) = 1.09 - 1.7x$ eV and $a(x) = 3 + 40x$ Å are determined by fitting the binding energies for two compositions near $x \simeq 0.35$. The resulting energies are depicted as heavy lines in Fig. 2, and considering the simplicity of the model, are in remarkable agreement with the data. Note that since this model neglects $\Gamma_1$-$X_1$ coupling, it is incapable of quantitatively describing the spectra near and beyond the direct-indirect crossover ($x \gtrsim 0.46$). Nevertheless, it does reproduce the nearly constant binding energy of $N_\Gamma$ and the approximately linear energy variation of $N_X$ throughout the range of direct-gap alloys.

It is noteworthy that a one-band, one-site Koster-Slater model used in the past produces only one bound state[6,11,21] and cannot describe the additional $N_\Gamma$ level; moreover, the Koster-Slater model cannot explain the linear dependence of the $N_X$ binding energy on composition, unless the strength of the potential is allowed to vary with $x$.[6] The present model is more satisfactory in that the potential is of nonzero radius and can support two electron bound states. Presumably the potential simulates a strain field surrounding the N impurity.[22] In the simplified effective-mass approximation used here, one state ($N_X$) has a momentum-space wave function peaked near $X_1$ with heavy-mass components which restrict the bound electron to the vicinity of the N center in real space. The other state ($N_\Gamma$) is comprised largely of light-mass $\Gamma_1$ components which allow the bound electron to be less localized spatially. Qualitatively, the weakly bound, delocalized $N_\Gamma$ state should couple only weakly to the lattice, whereas the confined $N_X$ state should interact strongly with the lattice. As expected, the spectra reveal prominent phonon sidebands of the $N_X$ line (Fig. 2), but no distinguishable phonon structure for the weak-coupling $N_\Gamma$ line. Finally, the model predicts that the $N_\Gamma$ state should enter the $\Gamma_1$ continuum at $x = 0.21$, in good agreement with the observations.

*Note added.*—The model used to account for the data of this work is basically phenomenological and does not apply beyond the restricted range $0.28 < x < 0.45$. Recently an extensive theory (G. G. Kleiman, unpublished) has been developed which is not restricted in range and which includes interactions between $N_\Gamma$, $N_X$, and $N$ (the short-range N trap).

We are grateful to M. G. Craford, W. O. Groves, and D. L. Keune (Monsanto Company, St. Louis) for generously providing the wide variety of crystals on which these studies depend.

*This work was supported by the Joint Services Electronics Program (U. S. Army, U. S. Navy, U. S. Air Force) under Contract No. DAAB-07-72-C-0259, by Monsanto Co., and by the National Science Foundation under Grants No. DMR-73-07661, No. DMR-72-03026, and No. DMR-72-03045-A01.

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## COMMENTS

# Comment on "Resonance Raman Scattering and Collision-Induced Redistribution Scattering in $I_2$"

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(Received 21 July 1975)

The form of resonant scattering spectra and their time decays are restated. An analysis of recent experimental results on molecular iodine shows that the existence of elastic collisional transfer processes cannot be positively proved.

In a recent Letter Rousseau, Patterson, and Williams (RPW) claim to present the "first experimental observation" of collisionally induced redistribution scattering.[1] This has been defined for resonance scattering of monochromatic light in gases[2] as the process by which *elastic* collisions between atoms redistribute the scattered radiation from the excitation frequency ($\nu_0$) over the absorption profile of the atomic resonance centered at $\nu_0 - \Delta\nu$. The effect of collisions on the form of resonance scattering spectra has long been recognized. In an early review[3] of the subject it was noted that in the limit of Doppler-broadened absorption lines the scattered light observed in a direction parallel to the direction of the exciting radiation has a spectral distribution which is closely related to that of the exciting radiation, e.g., if the exciting radiation is self-reversed, the emission line is also self-reversed.[4] However, when the absorption linewidth is dominated by collisional perturbations the emission line has exactly the same shape as the absorption line, whatever the excitation frequency or profile, and independent of the angle of viewing.[5] It was concluded that "the Rayleigh scattering persists only in those parts of the spectrum where the absorption caused by Doppler broadening or collision broadening of the absorption line practically vanishes."[3] These observations, together with the effect of *elastic* collisions, were fully included in the theory developed by Hüber to explain line shapes observed during resonant scattering of monochromatic light in gases.[2] There have been no experiments which demonstrate the elastic redistribution effect. Such an effect, and its dependence on $\Delta\nu$, may be of prime importance in theories describing the Raman effect.

It is the purpose of this paper to point out that the experiments performed by RPW[1] do not provide evidence for elastic collisional redistribu-