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Recombination processes involving Zn and N in $GaAs_{1-x}P_x$†

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Photoluminescence experiments have shown that for $GaAs_{1-x}P_x$:N,Zn in the direct composition region ($x \lesssim x_c \equiv 0.46$, 77 °K) the dominant radiative recombination process involves an electron bound to the N isoelectronic trap and a hole bound to the ionized Zn acceptor. In the indirect composition region ($x > x_c$), the influence of the Zn impurity on recombination is observed to decrease, and the dominant recombination process becomes the decay of bound excitons. This change in the radiative recombination process can be explained in terms of calculated optical-absorption coefficients for the competing transitions. The relative strengths of these absorption coefficients are compared to the shift (normalized) of the emission spectra obtained on p-type samples relative to the emission spectra obtained on n-type samples from the same $GaAs_{1-x}P_x$:N crystal prior to Zn diffusion.

INTRODUCTION

Recent experiments[1] have shown that in the direct composition region ($x \lesssim x_c \equiv 0.46$, 77 °K) the dominant radiative recombination process in $GaAs_{1-x}P_x:N^+$, Zn involves an electron trapped by the N isoelectronic impurity and a hole bound to the ionized Zn acceptor (referred to below as the "Zn-N transition"). This recombination process has been identified by comparing photoluminescence spectra obtained on n-type $GaAs_{1-x}P_x:N^+$ with spectra obtained from the same crystals after Zn has been introduced by dilute closed-tube diffusion.[1] In the region $x \lesssim x_c$, the entire spectra of the p-type samples, including the A line and NN-pair peak, are shifted to lower energy by approximately the Zn acceptor energy. The magnitude of the observed spectral shift is composition dependent, decreasing with increasing x near and beyond the direct-indirect transition ($x \equiv x_c$). In the indirect composition region ($x > x_c$) the Zn acceptor loses its influence, and the dominant radiative recombination process becomes the decay of bound excitons.

In previous work[2] we have employed a model based on the localization of the wave functions of the hole and electron in the Wannier representation to explain the weakening of the Zn-N transition relative to the bound exciton recombination process in the indirect composition region of $GaAs_{1-x}P_x$. In the present paper by means of a different procedure, we show that the results of our earlier work[1,2] can be obtained by calculating, for the $GaAs_{1-x}P_x$ alloy, the relative optical-absorption coefficient α for bound exciton and Zn-N transitions.

MODEL CALCULATIONS

Using the Golden Rule, we write for the transition rate for optical absorption

$$T_{fi}(\omega) = \frac{2\pi}{\hbar} \left| \langle f | V | i \rangle \right|^2 \delta(\hbar\omega - \hbar\omega_0), \qquad (1)$$

where

$$\hbar\omega_0 = E_f - E_i .$$

If quadratic terms in the vector potential $\vec{A}$ are neglected and the one-electron approximation is assumed, the perturbation term V is

$$V = \frac{e}{mc} \vec{A} \cdot \vec{p} . \qquad (2)$$

The vector potential for incoming radiation can be written as

$$\vec{A} = \sum_\lambda A_{0\lambda} e^{i(\vec{k}_\lambda \cdot \vec{r} - \omega_\lambda t)} \hat{n}_\lambda , \qquad (3)$$

where λ simply denotes the polarization direction. The initial and final states are the hole and electron states denoted as Ψ_h and Ψ_e, respectively. These wave functions can be expanded in terms of the Bloch functions, $\psi_n(\vec{k}, \vec{r})$, yielding

$$\Psi = \sum_n \int_{BZ} d^3k\, \phi_n(\vec{k})\, \psi_n(\vec{k}, \vec{r}) . \qquad (4)$$

Considering only dipole transitions and substituting Eqs. (2)–(4) into Eq. (1), we obtain for the transition rate for optical absorption

$$T_{fi}(\omega) = \frac{2\pi e}{\hbar mc} \sum_\lambda \sum_{cv} |A_{0\lambda}|^2 \left| \int_{BZ} d^3k\, \phi_e^*(\vec{k})\, \phi_h(\vec{k}) \langle c\vec{k} | p | v\vec{k} \rangle \right|^2 \delta(\hbar\omega - \hbar\omega_0), \qquad (5)$$

where $\langle c\vec{k}|p|v\vec{k}\rangle$ is a Bloch function matrix element corresponding to $\hat{n}_\lambda \cdot \vec{p}$. The summation on c and v can be eliminated by considering only the highest-energy valence band and the lowest-energy conduction band.

The optical-absorption coefficient is proportional to the transition rate and using Eq. (5) can be written

$$\alpha(\omega) = C_0\omega^{-1}\left|\int_{BZ} d^3k\phi_e^*(\vec{k})\phi_h^*(\vec{k})\langle c\vec{k}|p|v\vec{k}\rangle\right|^2 \times \delta(\hbar\omega - \hbar\omega_0), \qquad (6)$$

where C_0 is a constant. To evaluate the optical-absorption cross section for GaP : N, Faulkner[3] has argued that since the hole wave function is concentrated at $\vec{k}=0$, the Bloch function matrix element and the electron wave function can be evaluated at $\vec{k}=0$ and can be removed from the integral, yielding

$$\alpha(\omega) = C_1\omega^{-1}\left|\phi_e(0)\right|^2\left|\int_{BZ} d^3k\,\phi_h(\vec{k})\right|^2 \times \delta(\hbar\omega - \hbar\omega_0). \qquad (7)$$

While this approximation appears to be valid for the binary GaP : N, it breaks down for a certain range of crystal compositions when extended to the case of the ternary $GaAs_{1-x}P_x$: N (or $In_{1-x}Ga_xP$: N). As the crystal composition x is adjusted to bring the Γ conduction-band minimum close to the N trap energy ($E_\Gamma \to E_N$),[4] the electron wave function becomes more localized at Γ, and the assumption that the wave function of the hole is much more localized near $\vec{k}=0$ than that of the electron is no longer valid. Before proceeding, we shall investigate the range of crystal compositions for which the approximation leading to Eq. (7) is valid.

The Koster-Slater one-band one-site model has been used previously to evaluate the wave function of the trapped electron in GaP : N,[3] $GaAs_{1-x}P_x$: N,[2,5] and $In_{1-x}Ga_xP$: N[6,7] and can be employed in the present analysis. Accordingly, the modulus of the wave function of the electron can be written in the general form

$$|\phi_e(\vec{k})|^2 = \frac{|A|^2}{|\epsilon_c - E_N|^2}, \qquad (8)$$

where ϵ_c is the conduction-band energy. The normalization constant A depends on the N trap energy and the structure of the conduction band. Consequently A is a function of the crystal composition x.

Since the hole is bound by a Coulomb potential for both the bound exciton and Zn-N transitions, we assume a hydrogenic wave function for the hole state. Thus, the modulus of the hole wave function is given by

$$|\phi_h(\vec{k})|^2 = (4/\pi)^2 a_0^{-5}(k^2 + a_0^{-2})^{-4}, \qquad (9)$$

where a_0 is the screened Bohr radius. Equations (8) and (9) can be combined to show that the approximation leading to Eq. (7) is valid when

$$0.189(m_h^*/m_{e\Gamma}^*)[E_h/(E_\Gamma - E_N)] < 1. \qquad (10)$$

E_h is the binding energy of the hole measured relative to the valence band. The effective masses associated with the bound hole and the conduction-band electrons at Γ are m_h^* and $m_{e\Gamma}^*$, respectively. For the case of $GaAs_{1-x}P_x$: N, Zn at 77 °K the relation in Eq. (10) restricts calculations to crystal compositions in the range $x \gtrsim 0.4$. With this limitation in mind, we proceed to evaluate the absorption coefficients for the bound exciton and Zn-N transitions.

For the wave functions of the excitonic hole and the hole bound to the Zn acceptor, we use a 1s hydrogenic wave function. The screened Bohr radii for the excitonic hole and the Zn bound hole are denoted as a_{ex} and a_z, respectively. The energy of the bound-exciton transition is $\hbar\omega_0 = E_N - E_h^{ex}$. Similarly for the Zn-N transition we have $\hbar\omega_0 = E_N - E_h^{Zn} + E_c$, where $E_c \ll E_{Zn}$ is a measure of the Coulomb interaction between the electron and hole. Since the trapped electron is confined to the immediate vicinity of the N atom, the wave function of the excitonic hole is centered on the N site. For the case of the hole bound to the Zn acceptor, the hydrogenic wave function must be multiplied by an additional phase factor $e^{i\vec{k}\cdot\vec{R}_0}$ to account for the separation between the Zn and N impurities.

It is convenient to define a quantity γ as the ratio of the optical-absorption coefficient for the Zn-N

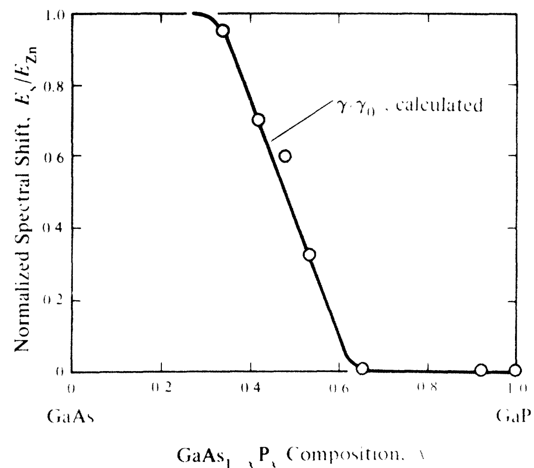

FIG. 1. Normalized spectral shift of the NN-pair peak versus crystal composition x (circles). Here E_s is the experimentally observed spectral shift, and E_{Zn} is the binding energy of the Zn acceptor. The solid curve has been obtained by normalizing γ at $x = 0.3$ and by adjusting a_{ex} to fit the data.

transition to that for the bound exciton transition. Evaluation of the integral in Eq. (7) using the wave functions discussed above yields

$$\gamma \equiv \alpha_{Zn}/\alpha_{ex} = (a_{ex}/a_z)^3 e^{-2R_0/a_z}. \qquad (11)$$

DISCUSSION

We note that Eq. (11) is identical to Eq. (18) in Ref. 2 where we compared the probability density, in the central cell of a N atom, for a hole bound to a Zn acceptor to the probability density for an excitonic hole. Thus, we conclude that the model based on the localization of the wave functions of the hole and electron yields the same result as a calculation of the strength of the absorption coefficient for the Zn-N transition relative to that of the bound exciton process.

As pointed out in Ref. 2, γ will decrease exponentially in the indirect composition region due to the increased binding energy of the Zn acceptor for $x \gtrsim x_c$. Accordingly, the Zn-N transition becomes weaker in the indirect region ($x > x_c$). This behavior is further accentuated by the fact that a_{ex} decreases for $x \gtrsim x_c$ owing to the decreased influence of the light-mass Γ conduction-band minimum. The fact that γ depends explicitly on the separation between the Zn and N atoms, R_0, indicates that the magnitude of the spectral shift should be a function of the densities of the Zn and N impurities.

Our results are summarized in Fig. 1, where the normalized spectral shift E_s/E_{Zn} (circles) is plotted versus the $GaAs_{1-x}P_x$ crystal composition x. In the direct composition region, the Zn-N transition dominates. For $x \gtrsim x_c$, however, the bound exciton transition is stronger and for $x \gtrsim 0.65$ $E_s/E_{Zn} \sim 0$. For comparison we have plotted γ/γ_0 (solid curve) where γ_0 is the value of γ at $x \sim 0.3$ and a_{ex} is regarded as a variable parameter. Both the data and the calculated curve indicate that there is a change in the recombination process near the direct-indirect transition in Zn-doped $GaAs_{1-x}P_x$:N. We note that our data and calculations are consistent with the known behavior of $GaAs_{1-x}P_x$:N, Zn[8] ($x \gtrsim 0.8$) and GaP:N.[9,10]

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