Isoelectronic impurity states in GaAs:N

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Using the one-band one-site Koster-Slater model, we explain the different behavior of isoelectronic impurities in GaAs:N and GaP:N in terms of their band-structure difference. We show that the two lowest nitrogen bound states, NN$\text{1}$ and NN$\text{2}$, are associated with the [220] and [110] nitrogen pairs, respectively, that the optical transition of the former is dipole allowed whilst the latter is forbidden in both systems, and that the order of the [220] and [110] pair levels are reversed in the two systems.

In 1965, Thomas, Hopfield, and Frosch$^1$ showed that nitrogen pairs with different separations gave rise to a series of excitonic emission lines in GaP:N. These transitions have since then been labeled as NN$\text{1}$, NN$\text{2}$, ..., NN$\text{10}$ in a sequence of reducing binding energy. These emission lines fall in a range of 150 meV below the fundamental band edge of GaP and converge to that of the isolated nitrogen center 11 meV below the free-exciton band edge. The authors associated the pair centers with the largest binding energy to the first nearest-neighbor pair [110], the second largest binding energy to the second-nearest-neighbor pair [200] and so on, based on the intuition that the closer the two nitrogen atoms, the larger the binding energy of the pair. There were neither microscopic techniques nor theoretical models available for confirming these assignments at that time. Faulkner$^2$ made the first attempt to calculate the nitrogen bound states in GaP:N in the framework of a short-range impurity potential model. He found that because of the interwell interference effects in such an indirect-gap system, the calculated order of the energy levels for the nitrogen pairs differed greatly from that given in Ref. 1. More specifically, the nearest-neighbor pair [110] did not have the largest binding energy. Instead, the [220] pair (the fourth-nearest pair) was found to have the largest binding energy and the optical transition between this bound state and the valence band was dipole allowed. The pair configuration with the second largest binding energy was the [110] and this transition was dipole forbidden. These results qualitatively agreed with the experimental results of Ref. 1, except for the fact that there the two lowest bound states were assigned to the [110] and [200] pairs originally. Here an allowed transition implies that the bound state has a nonzero component of $k$=0 conduction-band state, and a forbidden transition implies that the $k$=0 component is zero. A few later calculations, either with more complicated or simpler approaches,$^3$-6 have yielded qualitatively similar results to that of Faulkner. The shortcoming of these calculations was the negligence of the lattice relaxation and the accompanying strain field. A different point of view was provided by Allen,$^7$ who suggested that the nitrogen-nitrogen interaction was a strain effect, i.e., the strain field of one nitrogen atom altered the energy of an exciton bound to another nitrogen atom. In this model, the binding energy was proportional to $K_\text{NN}$ (here $K_\text{NN}$ is the pair separation), which could fairly well describe the experimental results. However, without considering the strain and ignoring the intervalley interference effect, Benoit à la Guillaume$^8$ also obtained an approximate $R_\text{NN}^{-3}$ dependence. The only theoretical calculation that considered both the short-range impurity potential and the lattice relaxation was performed by Shen, Ren, and Dow,$^9$ and this has been the only model that yielded exactly the same ordering of pairs energy wise as originally proposed by Thomas, Hopfield, and Frosch.$^1$ However, this model did not address an important issue as to whether or not the lattice relaxation could reverse the selection rule, since without the lattice relaxation the bound states associated with the [110] pair is forbidden, whereas that associated with the [200] pair is allowed, but experimentally one observes that NN$\text{1}$ is allowed and NN$\text{2}$ is forbidden.

The situation for GaAs:N is somewhat different from that for GaP:N. Kleinman predicted that the isolated nitrogen center would be a resonant state at $\sim$300 meV above the conduction-band edge of GaAs (the $\Gamma$ point).$^{10}$ Experimentally, Wolford et al. found this resonant state to be 150–180 meV above the $\Gamma$ point.$^{11}$ Two nitrogen-related transitions were reported by Schwabe et al.$^{12}$ in a relatively high-nitrogen-doped sample at 12 and 7 meV below the free-exciton band edge, and the deeper center showed a much weaker transition intensity compared to the shallower one. The higher energy transition was first attributed to the isolated nitrogen center.$^{12}$ Later, it was identified by Liu et al.$^{13}$ to be a N pair center. Based on the fact that the symmetry of this state was the same as that of NN$\text{1}$ in GaP:N, it was labeled as “NN$\text{1}$.” They also labeled the lower bound state to be “NN$\text{2}$,” because of its low emission intensity similar to NN$\text{2}$ in GaP:N. More recently,$^{14}$-16 other controversial assignments have been made for these nitrogen-related below-gap transitions. In contrast to the situation for GaP:N, the Shen et al. calculation$^7$ showed that the [110] pair was the only nitrogen-pair center that generated a bound state in GaAs:N.

There are a few questions that yet remain to be answered for GaAs:N: (1) Are the assignments of Ref. 13 correct? If yes, (2) Do the two nitrogen-pair bound states have the same configurations as those in GaP:N? (3) Why does NN$\text{2}$ have a larger binding energy than NN$\text{1}$? A more general issue that has not been addressed is the physical origin underlying why GaAs:N is so different from GaP:N. In this work, we make an attempt to answer the above-mentioned questions by employing a simple theoretical model, the so called one-band one-site Koster-Slater model,$^2$ to calculate the nitrogen-related states in GaAs:N.
The impurity state of a short-range impurity potential is often described as a solution of the following Green’s function equation:

\[ JG(E) = 1, \tag{1} \]

where \( G(E) \) is the Green’s function defined as

\[ G(E) = \frac{\Omega}{(2\pi)^3} \int_{BZ} \frac{dk}{E - E_g(k)}, \tag{2} \]

and \( J = 0 \) is the matrix element of the impurity potential for the Wannier function of the relevant band and centered at the impurity site. A bound state exists only if the following condition is satisfied:

\[ |J| \leq 1, \tag{3} \]

where \( E \) is defined by

\[ \frac{1}{E} = \frac{\Omega}{(2\pi)^3} \int_{BZ} \frac{dk}{E - E_g(k)}. \tag{4} \]

While \( J \) represents the potential strength, \( E \) represents the threshold for the kinetic energy. The Brillouin zone is divided into three regions associated with \( \Gamma, L, \) and \( X \) minima around which the energy dispersion is approximated to be parabolic with a finite extent. The relevant band-structure parameters are \( m_{f} = 0.067, m_{l} = 0.299, \) and \( m_{x} = 0.85 \) for the effective masses, and \( E_{L} = 300 \) meV and \( E_{x} = 460 \) meV for the conduction-band minima (with the \( \Gamma \)-point band edge as the energy reference). We find that (1) the [220] state is indeed dipole allowed; (2) the [110] pair has a binding energy of 15.7 meV and is dipole forbidden; (3) the isolated center has a resonant state at 106 meV above the \( \Gamma \) point; and (4) all the other pairs states are also resonant. Qualitatively, these results are in agreement with the experimental results. The two primary parameters are \( J = -3.5 \) eV and \( 1/E = 2.17 \times 10^{-4} \) eV^{-1}. Because of \( |J|/E < 1 \), the isolated nitrogen center is unable to form a bound state. Figure 1 shows a comparison of our calculated energy levels with the experimental results.
apply in GaAs:N. Although the electronegativity difference between N and As is even larger than that between N and P, and the pseudopotentials for P and As are similar, yet a bound state for the isolated nitrogen center is not observed in GaAs:N. A major reason for the different behavior of nitrogen impurities in GaP and GaAs is that the GaAs Γ point effective mass is much smaller than the GaP X-point effective mass: an impurity state tends to have a large kinetic energy and it is less easy to form a bound state if the conduction band has a small effective mass. In fact, the electron binding energy for the isolated nitrogen center in GaP:N has been determined to be ~6 meV, which corresponds to \( J = -1.8 \text{ eV} \). This value is smaller than that for nitrogen in GaAs that we derived above.

The 7-meV nitrogen-related bound state in GaAs:N has recently again been associated with the isolated nitrogen center. However, the fact that the isolated nitrogen center in GaP:N (Ref. 1) and the resonant state in GaAs:N (Ref. 11) both do not show a nitrogen local vibration-mode-induced phonon sideband while the nitrogen pairs in GaP:N (Ref. 1) and the two bound states in GaAs:N (Ref. 12) all show the local-mode phonon sideband makes the assignment of Ref. 16 unlikely to be valid.

In summary, we have applied the Koster-Slater model to GaAs:N. Assuming the experimentally observed 7-meV bound state corresponding to the [220] pair, we have found that the other derived N bound or resonant states agree with experimental results of Refs. 11 and 13 in terms of either the order of the energy levels or the selection rules. The two lowest bound states labeled as NN1 and NN2 in both GaP:N and GaAs:N are associated with the same pair configurations, i.e., [220] and [110], respectively. The conduction-band X valley that has the largest density of states plays an important role in determining positions of the N impurity states. It is the band-structure difference, i.e., the X valley being the highest and Γ valley being the lowest in GaAs and the reverse in GaP, which leads to the fact that an isolated N center generates a bound state in GaP:N but a resonant state in GaAs:N, and the difference in the level order of the [220] (NN1) and [110] (NN2) pairs in GaP:N and GaAs:N.

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