Isoelectronic impurity states in GaAs:N

Yong Zhang and A. Mascarenhas

National Renewable Energy Laboratory, Golden, Colorado 80401

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_1 and NN_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 $NN_1, NN_2, \ldots NN_{10}$ 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 intervalley 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 R_{NN}^{-3} (here R_{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_{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[2] 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_1 is allowed and NN_2 is forbidden.

The situation for GaAs:N is somewhat different from that for GaP:N. Kleiman predicted that the isolated nitrogen center would be a resonant state at ~ 300 meV above the conduction-band edge of GaAs (the Γ point).[10] Experimentally, Wolford *et al.* found this resonant state to be 150–180 meV above the Γ 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_1 in GaP:N, it was labeled as ''NN_1.'' They also labeled the lower bound state to be ''NN_2,'' because of its low emission intensity similar to NN_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[9] 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_2 have a larger binding energy than NN_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:[2,17]

$$JG(E)=1, \tag{1}$$

where $G(E)$ is the Green's function defined as

$$G(E) = \frac{\Omega}{(2\pi)^3} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{E - E_c(\mathbf{k})}, \tag{2}$$

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:[2,17,18]

$$|J|/\bar{E} \geqslant 1, \tag{3}$$

where $\bar{E}$ is defined by

$$\frac{1}{\bar{E}} = \frac{\Omega}{(2\pi)^3} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{E_c(\mathbf{k})}. \tag{4}$$

While J represents the potential strength, $\bar{E}$ represents the threshold for the kinetic energy.[18] $\bar{E}$ depends strongly on the effective mass or dispersion of the band. For a nitrogen pair with one atom located at the origin and the other at $\mathbf{R}_m$, the corresponding equations are

$$J[G(E) \pm G(E,\mathbf{R}_m)] = 1, \tag{5}$$

where $G(E,\mathbf{R}_m)$ is defined as

$$G(E,\mathbf{R}_m) = \frac{\Omega}{(2\pi)^3} \int_{\mathrm{BZ}} \frac{\exp(i\mathbf{k}\cdot\mathbf{R}_m)d\mathbf{k}}{E - E_c(\mathbf{k})}. \tag{6}$$

If the impurity level is resonant in the conduction band, E is allowed to have an infinitesimal positive imaginary part.[17]

We first assumed that the experimentally observed shallowest nitrogen pair transition[12,13] at 7 meV below the GaAs band edge corresponds to the same pair configuration as the NN_1 center in GaP:N, i.e., the [220].[2–5] The GaAs conduction band is described in a rather simplified manner as in the treatment by Kleiman:[19] the Brillouin zone is divided into three regions associated with Γ, L, and X minima around which the energy dispersion is approximated to be parabolic with a finite extent. The relevant band-structure parameters are $m_\Gamma = 0.067$, $m_L = 0.299$, 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 Γ-point band edge as the energy reference).[20] 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 Γ point; and (4) all the other pairs states are also resonant. Qualitatively, these results are in agreement with the experimental results.[11–13] The two primary parameters are $J = -3.5$ eV and $1/\bar{E} = 2.17 \times 10^{-4}$ eV^{-1}. Because of $|J|/\bar{E} < 1$, 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.
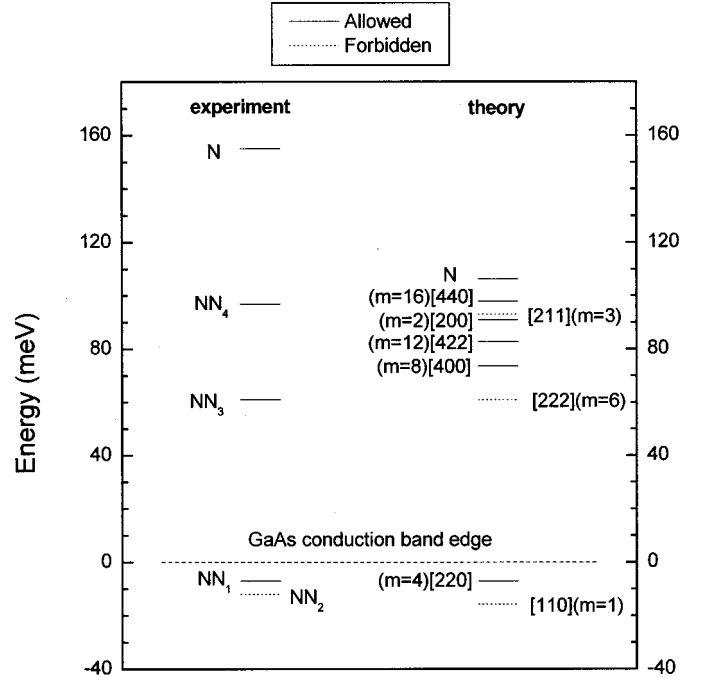

FIG. 1. Impurity states of an isolated nitrogen atom and nitrogen-atom pairs in GaAs:N. m stands for the shell number of the pairs ($m = 1,2,\ldots$ correspond to the first-nearest neighbor, the second-nearest neighbor, and so on) (Ref. 22).

It appears that even though GaAs is a direct-gap semiconductor, the intervalley interference effect is still significant. The contribution to the X valley remains especially important in determining the relative energy positions of the pairs. In GaP:N, it is because of the sign difference of the interference factor $f(X)$ for the X valley [$f(X) = -1$ for the [110] pair and 3 for the [220] pair[2]] that the [110] pair is a forbidden and the [220] pair is an allowed bound state. Our calculation indicates that the same reasoning holds true for GaAs:N, because of the largest density of states of the X valley. However, the ordering of the two pair states depends on the detailed properties of the band structure. The [110] pair happens to be lower than the [220] pair in GaAs:N, because of a relatively weaker destructive interference of the X valleys in this case. If we associated the experimentally observed allowed bound state with the second-nearest-neighbor pair [200], we would have more allowed pair states, i.e., the [220], [400], and [422], located below the [200] pair, and a forbidden state, i.e., the [110] pair, with a 120 meV binding energy, which is contrary to the experimental result.

An apparent shortcoming of our model calculation is the negligence of the lattice relaxation as mentioned above. Lattice relaxation has to be considered in a refined theory. However, we believe that the lattice relaxation should not change the results qualitatively, based on the fact that this model is able to provide not only the correct ordering of energies but also the selection rules for the two lowest bound states in the two systems.

The binding mechanism underlying the formation of the isoelectronic impurity bound state in GaP was explained in terms of the electronegativity[1] or atomic pseudopotential[18] difference between N and P. However, these rules do not

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 $J = -1.8$ eV.[21] 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.[16] 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 NN_1 and NN_2 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] (NN_1) and [110] (NN_2) pairs in GaP:N and GaAs:N.

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