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# Impurity perturbation to the host band structure and recoil of the impurity state

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At sufficiently high doping levels, the impurities in a semiconductor are expected to perturb the host band structure, and the perturbed host is then expected to alter the impurity state from that of the dilute limit (a recoil). Despite many decades of studies on impurities, it has been impossible to *simultaneously* and *accurately* track the evolution of the host band structure and the impurity state. The isoelectronically doped system provides a unique opportunity to track this evolution. GaAs:N, as a prototype system, has been investigated both experimentally and theoretically for this purpose.

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Impurities in semiconductors have been studied for over five decades.[1–5] The impurity introduces a perturbation into the host band structure, and in turn the modification of the host should affect the impurity state (a recoil). When quoting an experimentally measured energy state for a specific impurity in a semiconductor, one implies that the sample is in a ‘‘dilute doping limit’’ such that the doping does not cause any change to the host and that there is no impurity-impurity interaction. Although, for the most well studied *Coulombic impurities*, shallow donors and acceptors, it is well known that an increase of the doping level beyond the ‘‘dilute doping limit’’ leads, first, to a line broadening,[6,7] and subsequently to a band gap reduction,[5] due to impurity band formation. However, *simultaneously* tracking the evolution of the *impurity level* and the *host band structure* has been hitherto found to be very difficult, if not practically impossible.[8]

We demonstrate here that isoelectronic impurities can provide a real opportunity for a precise tracking of the impurity-host interaction. Recently, an intense effort has been devoted to understanding the electronic properties of nonconventional semiconductor alloys (e.g., GaAs:N and GaP:N) that are formed by heavy isoelectronic doping.[9–13] GaAs:N is particularly interesting, because although the N doping leads to a continuous modification of the host band structure, resembling the situation of a typical conventional alloy, the doping also introduces various highly localized and bound states. For the reasons given below, the energy shifts of the sharp GaAs band edge excitonic absorption and nitrogen bound exciton emission can be accurately monitored with varying N doping concentrations. Not only does such a study offer an insight into the evolution of this nonconventional alloy, but it also sets up a benchmark for testing the theoretical modeling of this type of system, and enhances our understanding of the behavior of impurities in semiconductors in general.

There is a close similarity between Coulombic and isoelectronic impurities. The picture of the electronic structure of an isoelectronic bound exciton has been well established in early studies of the isoelectronic impurities in the dilute doping limit.[14–16] In the one-electron picture, for the case of GaAs:N, it can be approximately described by an electron bound state with a binding energy $E_e$ below the conduction band, which acts as a negative center for attracting the hole, and an accompanying hole bound state with a binding energy $E_h$ above the valence band.[16] Because of the similarity between this bound exciton state and an acceptor, the former is known as an acceptorlike bound exciton.[14] However, there exists an important difference between the negative charge centers $N^-$ and $A^-$. The $N^-$ state only appears with an external excitation, whereas $A^-$ exists spontaneously. For the Coulombic impurity, the relatively weak central cell impurity potential makes the host semiconductor, to a large extent, behave as an inert dielectric continuum.[4] The many-particle Coulomb interactions among the excess charges tend to cause a rapid line broadening which can overwhelm the energy shift of the impurity state and the band edge. There are thus two singular advantages in the isoelectronic system that makes a close tracking of the impurity-host interaction feasible. First, because of the absence of the excess charges prior to an external excitation, the many-particle Coulomb interaction is negligible under a weak optical excitation. Second, its central cell potential provides a much stronger perturbation to the host band structure.

Here we report high precision low temperature absorption and photoluminescence (PL) measurements for a set of free standing $\mathrm{GaAs}_{1-x}\mathrm{N}_x$, samples with $x$ being accurately determined. The shifts of the N induced bound states are tracked simultaneously with the shift of the band gap by systematically varying $x$ in small steps (with $\sim 15$ samples in the region $x < 0.1\%$), and their identities are verified by their characteristic magnetic field dependence. Surprisingly, nitrogen doping induced band gap reduction is found to be detectable even at very low N concentrations, and this is confirmed theoretically by applying a newly developed motif based charge patching method for the band structure calculation of this nonconventional alloy.[17] For a large impu-

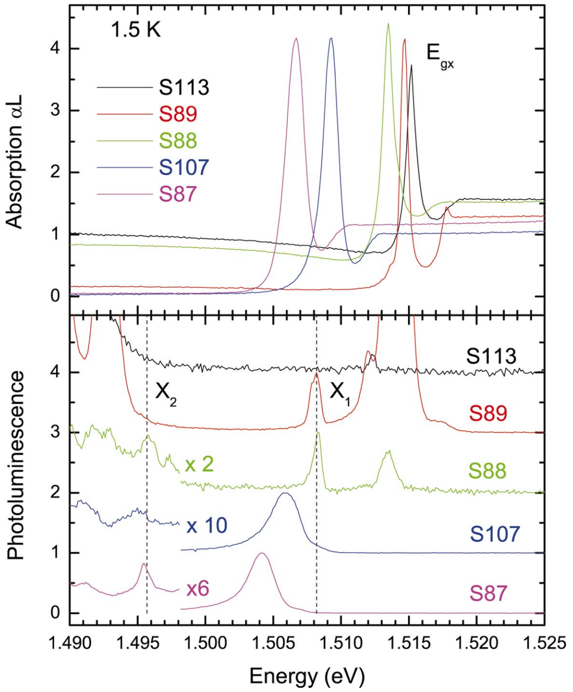

FIG. 1. (Color) Low temperature absorption and PL spectra for GaAs:N samples with varying N concentrations: S113-$(7\pm3)\times10^{15}$; S89-$(3.15\pm0.28)\times10^{17}$; S88-$(9.5\pm0.6)\times10^{17}$; S107-$(3.58\pm0.12)\times10^{18}$; S87-$(5.40\pm0.23)\times10^{18}$, in $\mathrm{cm}^{-3}$. All PL spectra are scaled to the intensity of the $X_1$ line. $X_2$ is too weak to be seen for S89.

rity structure, this method is able to produce an accurate charge density similar to that of a self-consistent calculation, but without actually doing the impermissible self-consistent calculation for the large structure.

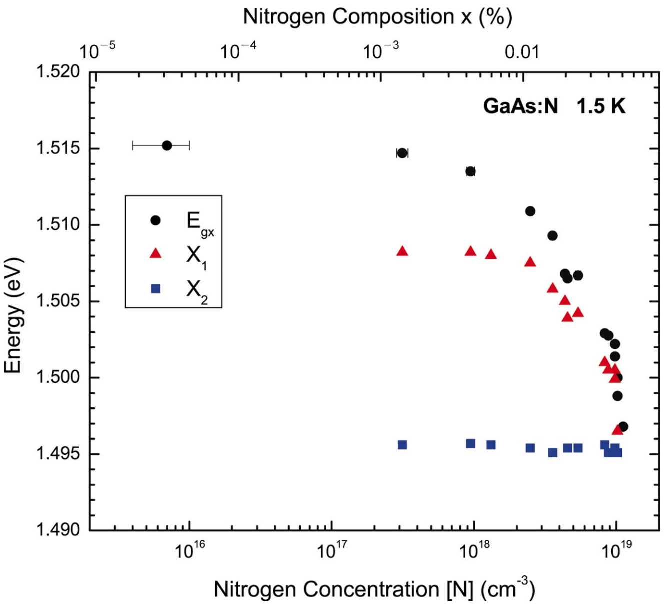

FIG. 2. (Color) The dependence of the energy level on N concentration. $E_{gx}$- the hostlike band edge excitonic absorption peak, $X_1$- the first nitrogen pair bound exciton state, and $X_2$- the second nitrogen pair bound exciton state.

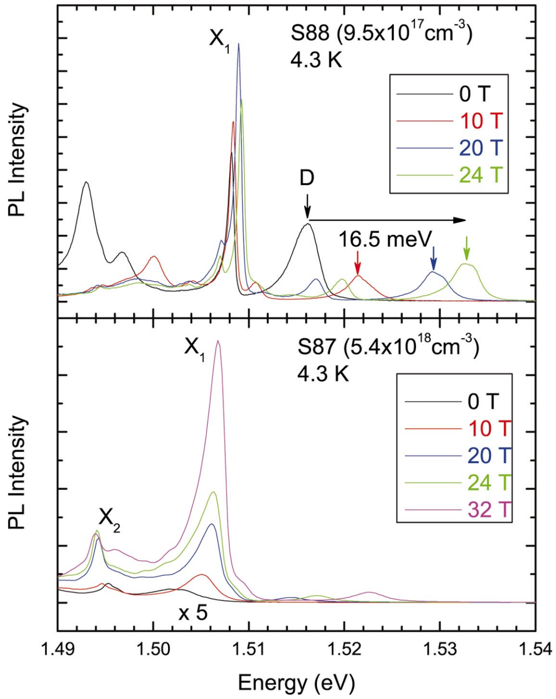

FIG. 3. (Color) M-PL for two GaAs:N samples with a varying magnetic field strength, with one sample (S88) in the dilute doping region and the other one (S87) in a higher doping level that already shows a shift of $X_1$ with the band gap change (the recoil effect).

GaAs:N samples were grown by low pressure metal-organic chemical vapor deposition on S.I.-GaAs substrates. An 80-nm AlAs layer was inserted for lifting off the epilayer by chemical etching. The nominal epilayer thickness is 1 $\mu$m. The transmission and PL were measured at 1.5 K on the same spot of a free standing film that was glued at its edge to a thin metal wire. The spot size is $\sim$50 $\mu$m. The excitation density is $\sim1-3$ W/cm$^2$. The spectra were measured using a system with a Spex270 spectrometer and a CCD detector, with a typical resolution of 0.4 meV. A sub-meV relative shift of the spectral lines between the undoped and doped samples can be reliably measured. Magneto-PL (M-PL) spectra were measured at 4.3 K on a CCD spectroscopy system with magnetic fields up to 32 Tesla. The N concentration [N] was measured by secondary ion mass spectrometry (SIMS) with a background detection limit of $3\times10^{15}$ $\mathrm{cm}^{-3}$. The residual doping for donors (Si and Se) and acceptors (C and Zn) is below $5\times10^{15}$ $\mathrm{cm}^{-3}$ as measured by SIMS.

Figure 1 shows the absorption and PL spectra for several GaAs:N samples. The reference is a nominally undoped sample (S113) with a background N level of $(7\pm3)\times10^{15}$ $\mathrm{cm}^{-3}$. Surprisingly, N doping results in a 0.5 meV reduction in the excitonic band gap $E_{gx}$ in a sample (S89) with [N] as low as $(3.2\pm0.3)\times10^{17}$ $\mathrm{cm}^{-3}$ ($x\sim1.4\times10^{-5}$) that would normally be considered well within the dilute doping limit. Two sharp PL peaks ($X_1$ and $X_2$), which emerge when $[\mathrm{N}]>10^{17}$ $\mathrm{cm}^{-3}$, are known to originate from excitons bound to nitrogen pair centers,[18,19] with the isolated N center forming a resonant state in the conduction band.[20] On increasing [N], with the band gap moving down, $X_1$ exhibits a redshift, but that for $X_2$ is far less significant. Concurrently, both the excitonic absorption peak and $X_1$ broaden. The band edge excitonic peak is found to be totally smeared out at $[\mathrm{N}]\sim 10^{20}\ \mathrm{cm}^{-3}$.[13] Figure 2 summarizes the [N] dependences of $E_{gx}$, $X_1$ and $X_2$ for all $x<0.1\%$ samples. We notice that since $X_1$ shifts quite differently from $E_{gx}$, it becomes nearly resonant with $E_{gx}$ at $[\mathrm{N}]\sim 10^{19}\ \mathrm{cm}^{-3}$. Such a difference is typical for a highly localized state that does not follow any particular band edge under a perturbation. While the N induced perturbation to the host occurs at $[\mathrm{N}]>10^{17}\ \mathrm{cm}^{-3}$, the recoil of the shallowest bound state $X_1$ becomes observable when $[\mathrm{N}]>10^{18}\ \mathrm{cm}^{-3}$. For deeper N related bound states ($X_2$ and others that are not discussed here[21]), the shifts are progressively smaller with increasing binding energy. Evidently, the nitrogen bound states do not remain fixed, to be passively swept away by the downward moving band edge, contrary to the prediction of a recent empirical pseudopotential calculation.[11]

To further confirm that the moving emission below the band gap indeed originates from $X_1$, we have performed M-PL under high magnetic fields, since a highly localized state like $X_1$ (for its electron bound state) is expected to respond very differently to the magnetic confinement as compared to either an extended band edge state or a weakly localized Coulombic impurity state that typically follows the band edge under any external perturbation. Figure 3 shows M-PL spectra for two typical samples. For the lower [N] sample S88, the magnetic shift of $X_1$ from 0 to 24 T is merely $\sim 1$ meV, which is substantially smaller than 16.5 meV for the Coulombic impurity related transition "$D$."[22] For the higher [N] sample S87, the peak assigned as $X_1$ indeed behaves like a highly localized state with a small magnetic shift, but the shift has increased to $\sim 3$ meV instead. The larger energy shift for the higher [N] sample indicates a delocalization effect due to the hybridization of the impurity state with the downshifting band edge state. The field induced $X_1$ intensity enhancement is due to the suppression of the energy transfer from $X_1$ to other deeper emission centers, which is more significant for the higher [N] sample. In addition, the shift of $X_1$ has been confirmed by the simultaneous shift of its characteristic phonon sideband (data not shown).

Since the primary interaction range for the bound exciton is the radius of the hole bound state that is somewhat larger than that of an effective mass acceptor,[23] the shift and broadening of the $X_1$ state could in principle arise from the wave function overlap of the hole bound state, just as for the acceptor. For the shallow acceptor in GaAs, the critical concentration for Mott transition is $n_c\sim 6.1\times 10^{17}\ \mathrm{cm}^{-3}$, corresponding to an effective Bohr radius of $\sim 64$ Å.[4,24] Although $[\mathrm{N}]=10^{19}\ \mathrm{cm}^{-3}$ corresponds to a typical pair concentration of $\sim 2.7\times 10^{16}\ \mathrm{cm}^{-3}$, the excitation density under a weak excitation (e.g., $1\ \mathrm{W/cm}^{-2}$) is estimated to be below $10^{14}\ \mathrm{cm}^{-3}$, which translates to an average exciton separation of 330 Å. Thus, under our experimental conditions, the shift and broadening of the bound exciton state are unlikely due to the Coulomb interaction. Only under a high excitation density will the isoelectronic system resemble the acceptor-doped system. In fact, GaAs:N can be employed for emulating the situation for an acceptor doping with a tunable acceptor concentration simply by varying the optical excitation density. Two other mechanisms, both related to the random distribution of the nitrogen impurities, are likely to be more important for the [N] dependence of the bound exciton state. The direct mechanism is that the N pair centers are not truly isolated centers any more, but perturbed differently by their environments. The indirect mechanism is that the alloy fluctuation of the band gap energy is manifested in the fluctuation of the impurity state energy, since the impurity state hybridizes with the approaching band edge state with increasing [N].

To quantitatively understand the band gap reduction observed in the very low doping region, we have performed a band structure calculation for GaAs:N, using a charge patch method.[17] This method is based on a self-consistent first-principles pseudopotential approach, in the framework of density functional theory within a local density approximation (LDA). Taking advantage of the high degree of charge density localization of the isoelectronic impurity, the self-consistent charge densities calculated for small prototype systems are transferred to a large system (with thousands of atoms) by reassembling charge motifs. Then, a folded spectrum method is used to solve the large system. The energy cutoff for the plane wave basis is 35 Ry. The valence force field method is used to relax the atomic positions, which has been shown to be an adequate approximation.[17] Corrections to the nonlocal potentials of the Ga, As and N atoms are introduced to fix the LDA error in band gaps as well as the intervalley separations ($\Gamma$-$L$ and $\Gamma$-$X$). The correct intervalley separations are essential to give correct intraband couplings caused by the impurity potential. As an approximation, we consider an ordered array with one N atom per supercell, instead of the random structure in a real sample. The supercell is a cubic box with a multiplication factor $n$ along three directions of the basic zinc-blende cubic cell, with $n$ varying from 3 to 10. Our calculation yields a resonant level for the isolated N center located 180 meV (by extrapolation) above the conduction band edge in the dilute limit, which is in excellent agreement with the experimental values.[20] A comparison of the calculated band gap reduction with the experimental data (with $x<0.5\%$) is shown in Fig. 4. The calculated curve is found to be sublinear with an exponent $\alpha\sim 0.9$ ($\delta E_g\propto x^{\alpha}$) in the region considered, whereas the experimental data shows a small bowing. An extrapolation of the calculated curve to the lowest [N] data point yields an exact match, thus providing a strong corroboration between experiment and theory. We believe that such a calculation offers an accurate account for the effect due to the isolated N centers distributed according to their average separation. Thus, the calculation is more accurate for the samples in the low doping region, as the formation of the pair states and their interactions with the host are more prominent at higher concentrations. Since the isolated N center forms a resonant state, the calculated structure is in fact similar to a conventional alloy like for example $\mathrm{GaAs}_{1-x}\mathrm{P}_x$. The primary difference here is that N introduces a much stronger perturbation to the host than P, and therefore a cluster as small as one N pair is able to generate a bound state. It

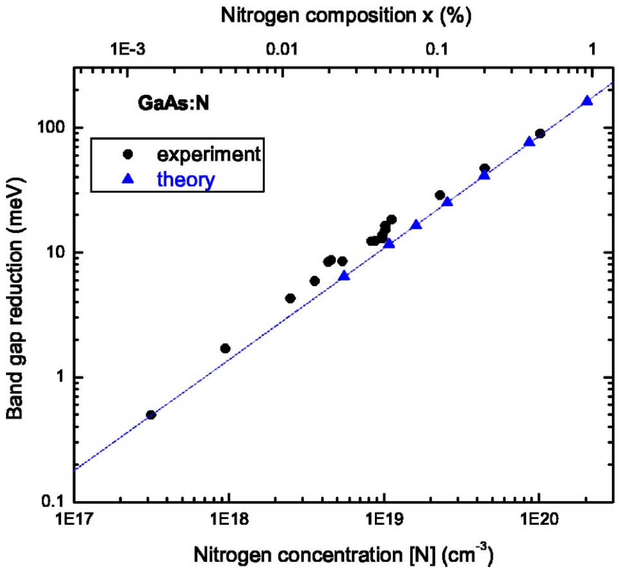

FIG. 4. The dependence of the band gap reduction as a function of N concentration: experimental data vs theoretical calculation.

is the formation of these small cluster bound states that makes $GaAs_{1-x}N_x$ behave abnormally,[21] as compared to the conventional alloy.

Although the recoil effect in GaAs:N has only been monitored for the bound states of N pairs, it is expected that those N induced states resonant above the conduction band edge also respond to the increase in N doping level. It is of particular interest as to how the resonant isolated N level, the primary contributor to the band gap reduction in the low [N] region, evolves with varying [N]. An above band gap transition (the so called $E_+$), widely observed in modulation spectroscopy, has been claimed to be due to the transition between the valence band and the isolated N state,[25] but its exact origin has been a subject of controversy.[11,26,27] Therefore, the obtained [N] dependence of the N pair bound state, together with that of the band gap, offers an invaluable test for scrutinizing the theoretical ability to model isoelectronic impurity systems and their related alloys.

In summary, for the first time, to our knowledge, the impurity-host interaction in a doped semiconductor has been measured in a precise manner such that both the impurity-to-host perturbation and the recoil of the impurity state can be simultaneously and unambiguously tracked. A band structure calculation, with near first-principles accuracy, for the impurity perturbation has been used to verify the experimental results. The study on the prototype system GaAs:N offers a valuable insight into the formation and evolution of the strongly mismatched alloy, and into the relevance of the physics of isoelectronic doping to that of Coulombic doping.

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