Excitons bound to nitrogen pairs in GaAs as seen by photoluminescence of high spectral and spatial resolution

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High resolution photoluminescence (PL) spectroscopy was performed on high quality bulk GaAs, lightly doped with the nitrogen isoelectronic impurity. The shallowest nitrogen pair bound exciton center labeled as X_1 revealed a total of six transitions. The photoluminescence lines from a small ensemble of nitrogen centers showed polarization dependent intensity. High spectral resolution PL spectroscopy was combined with confocal spectroscopy experiments performed on a GaAs:N/AlGaAs heterostructure. The high spatial resolution achieved by this technique enables us to localize and examine individual nitrogen bound excitons. Similar spectral structure and polarization dependence was observed for individual N-pair centers in GaAs. Both techniques support the C_{2v} symmetry of such isoelectronic impurity centers. The comparison between the PL spectra from an ensemble of nitrogen pairs and individual centers demonstrate the ability of the single impurity technique to lift the orientational degeneracy.

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I. INTRODUCTION

The physics of isoelectronic impurities has been the subject of numerous studies since their discovery.[1] In recent years, nitrogen doped GaAs and GaInAs have received considerable physical and technical attention due to their peculiar N-induced properties and potential for optoelectronic applications. The incorporation of a small amount of nitrogen leads to dramatic changes in the electronic band structure, such as a gigantic band gap reduction,[2,3] that has motivated the strong efforts to fabricate long wavelength lasers, high-efficiency multijunction solar cells, and heterojunction bipolar transistors. These energy and communication related applications have provided a strong motivation to the effort of understanding the evolution of the electronic structure from the very dilute phase of this unconventional alloy. In order to understand the nature of the electronic properties of nitrogen doped GaAs, a detailed study at different doping levels is necessary. At dilute doping, the N isoelectronic impurity introduces the resonant state N_x 150–180 meV above the GaAs conduction band minimum, which can be observed through the application of hydrostatic pressure.[4] When the nitrogen doping level is increased to 10^{16}–10^{17} cm^{-3}, below band gap N-related transitions can be observed which are thought to originate from nitrogen pair bound excitons. This assignment has been supported by theoretical calculations, and the photoluminescence (PL) transitions are referred to as NN_1 and NN_4 or X_1 and X_2.[5–7] As the N concentration reaches 10^{18}–10^{19} cm^{-3}, N-related levels appear in the band gap, which have been attributed to nitrogen cluster bound excitons.[8–11] These transitions can be exceedingly narrow.[12] Moreover, the emission associated with the GaAsN alloy band gap is observed to exhibit a rapid energy reduction and approach the N-related levels within the band gap with increasing nitrogen concentration.[10,13]

In this study, we focus on the PL transitions of excitons bound to N pairs labeled as X_1. A detailed analysis of its spectral components, site symmetry, and arrangements of the N atoms in the lattice will be presented. High spectral resolution spectra on an ensemble of N-pair bound excitons will be compared with spectra obtained from individual centers using a powerful technique introduced in Refs. 14 and 15 in relation to impurity centers and extensively used in the past to study single molecules and nanostructures.[16] The ability to observe single impurity bound excitons permits the observation of their intrinsic properties otherwise hidden by ensemble averaging.

II. SAMPLE AND EXPERIMENT

Samples used in the ensemble high resolution experiments were grown by metal organic vapor phase epitaxy. The epitaxial layer was 1 μm thick, grown on a semi-insulating GaAs substrate. The samples used in the single impurity study were grown by molecular beam epitaxy and consisted of a 25 nm GaAs:N layer, clad by a protective 5 nm GaAs layer on both sides and placed between two $Al_{0.25}Ga_{0.75}As$ barriers. The nitrogen concentration was measured by

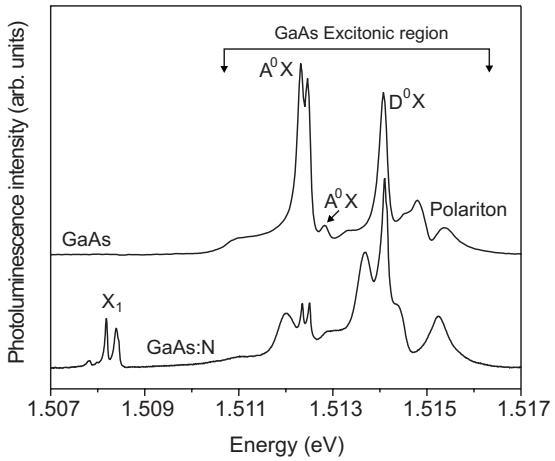

FIG. 1. Photoluminescence spectra of the GaAs and GaAs:N samples at 4.2 K showing the excitonic region. A^0X and D^0X label the neutral acceptor and donor bound excitons, respectively. The lower spectra obtained from the GaAs doped with nitrogen show the first transition of excitons bound to N pairs labeled in the literature as X_1.

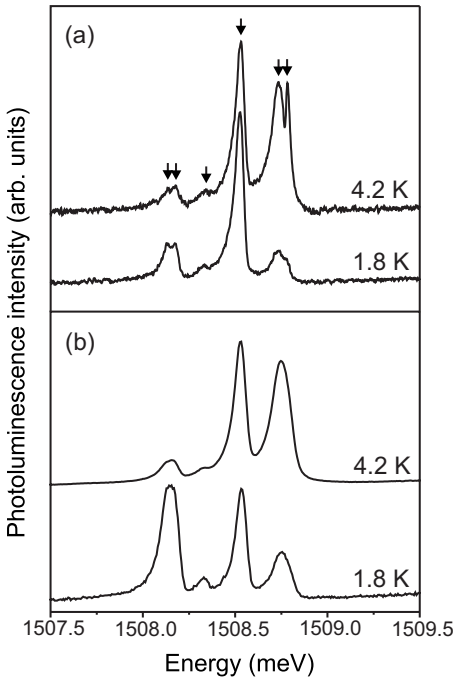

FIG. 2. Ensemble photoluminescence spectra of the exciton bound to nitrogen pairs X_1 at 4.2 and 1.8 K. In (a), six transitions can be resolved, marked by the vertical black arrows. By decreasing the temperature from 4.2 to 1.8 K, the higher energy transitions thermalize to the lower energy ones, indicating that all six transitions originate from the same center. This behavior can be better observed (b), where the excitation at 650 nm was provided by the dye laser. In order to improve the signal to noise ratio, the spectra in (b) were collected at a lower resolution; therefore, some of the spectral components have not been resolved.

secondary-ion mass spectroscopy on thicker calibration samples to be 3×10^5 μm^{-3}, corresponding to a pair surface density of 0.6 μm^{-2}. In the single impurity center study, the samples were mounted in a cold copper finger inside an Oxford high resolution microstat. Because of the long carrier diffusion length at 5 K, the spatial resolution for the detection of the photoluminescence is set by a 10 μm pinhole located in an intermediate image plane, resulting in a spatial resolution of 0.64 μm^2.[15] The emitted light was spectrally resolved with a grating spectrometer equipped with a liquid nitrogen cooled charged coupled device (CCD), resulting in a combined resolution of ~60 μeV. The ensemble high resolution PL spectra were collected with samples mounted in a strain-free manner and immersed in liquid helium. The detection system included a SPEX1403 double-grating spectrometer equipped with liquid nitrogen cooled CCD. The excitation at 650 nm was provided by a coherent dye laser using the RG6 dye and that at 800 nm with a Ti:sapphire laser. The polarization dependence of the emitted light was measured by rotating a wave plate and keeping the polarizer in front of the spectrometer slit fixed.

III. RESULTS AND DISCUSSION

In Fig. 1, PL spectra of pure GaAs and a moderately doped GaAs:N sample at 4.2 K are compared. Both samples show the usual excitonic region observed in bulk GaAs, the neutral acceptor bound exciton (A^0X), the neutral donor bound exciton (D^0X), and free exciton-polariton region. These transitions in GaAs have been thoroughly discussed in the literature.[17] The GaAs:N sample shows an additional transition labeled as X_1, attributed to excitons bound to nitrogen pairs. The single nitrogen level is resonant in the conduction band, and its bound exciton transitions can only be observed under high hydrostatic pressure.[4]

Two centers have so far been attributed to transitions originating from excitons bound to nitrogen pairs below the band gap, X_1 and X_2 at 1.5085 and 1.4986 eV, respectively.[5–7,15] High resolution ensemble spectra of the X_1 bound exciton center from the bulk GaAs:N sample were recorded and have been shown in Fig. 2. The six vertical arrows in the Fig. 2(a) indicate six transitions. By decreasing the temperature from 4.2 to 1.8 K, the higher energy transitions thermalize to the lower energy ones, indicating that all six transitions originate from the same center and resulting also in the enhancement of the lower energy doublet. Due to the lower excitation power and excitation energy, significantly better thermalization was achieved in the spectra shown in Fig. 2(b), greatly enhancing the lower energy transitions. Slightly lower spectral resolution was used to record these spectra in order to improve the signal to noise level.

We proceed by discussing the site symmetry of the nitrogen pairs and the implications to the spectra. The excitonic transitions observed in the PL spectra originate from electrons localized in the Γ_6 minimum of the conduction band, and the holes are associated with the top of the Γ_8 valence band. The exchange interaction or **J**-**J** coupling splits the $\Gamma_6\times\Gamma_8$ excitonic state into a $\mathbf{J}=1$ triplet and a $\mathbf{J}=2$ quintet. In the case of a single nitrogen impurity bound exciton, the crystal field of T_d symmetry ($\Gamma_6\times\Gamma_8=\Gamma_3+\Gamma_4+\Gamma_5$) leads to a

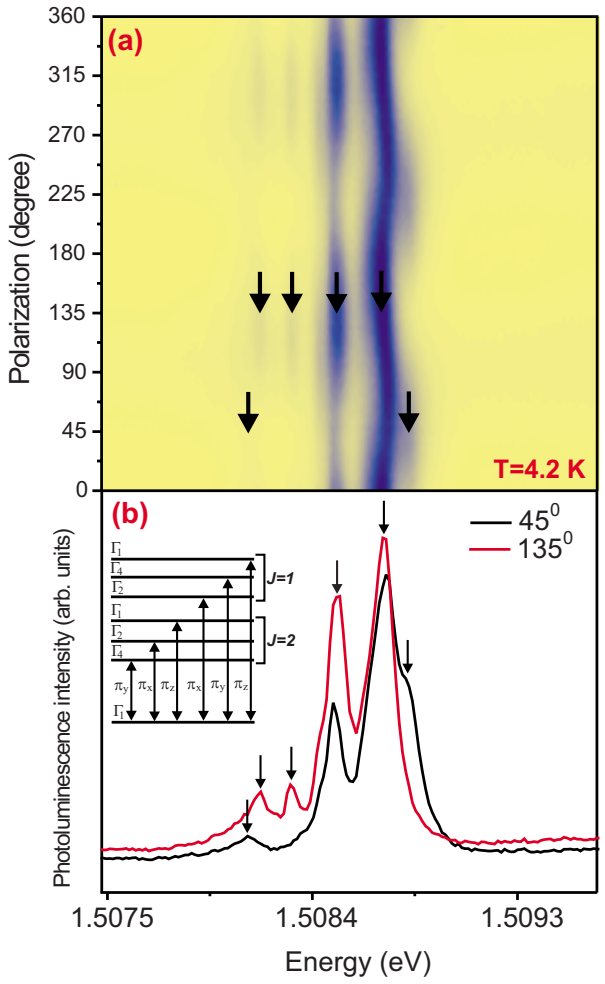

FIG. 3. (Color online) (a) Two-dimensional map of the polarization dependence of an ensemble of nitrogen pair bound excitons (X_1) at 5 K. The color PL intensity in arbitrary units increases from yellow (light gray) to blue (dark gray). The six vertical black arrows at 45°, 135° (four lines), and 45°, respectively, indicate the polarizations at which the transitions maximize. The number of the allowed transitions and their polarization behavior of the emitted light provide information about the symmetry of the center, i.e., the arrangement of the nitrogen atoms in the host lattice. (b) shows the spectra at the two crucial polarizations: 45° (black line) and 135° (red/gray line), with the vertical black arrows indicating the transitions. The inset in (b) shows the six allowed transitions corresponding to the C_{2v} center symmetry.

$\mathbf{J}=1$ like state Γ_5 and further splits the $\mathbf{J}=2$ like state into a Γ_3 doublet and a Γ_4 triplet. The local symmetry is further reduced for excitons bound to nitrogen pairs. Depending on the location of the nitrogen atoms in the lattice, the center can have C_{3v}, D_{2d}, C_{2v}, C_s, or C_2 local symmetry, which can lift the degeneracy partially or entirely. The transition diagram corresponding to a center of C_{2v} symmetry is shown in the inset of Fig. 3(b). Some of the pair configurations are thought to be resonant in the conduction band, and the only two bound state attributed to N pairs are the X_1 and X_2 centers. The center symmetry of nitrogen pairs has been discussed in detail for the nitrogen bound exciton transitions in GaP (Refs. 18 and 19) and GaAs.[15] Recently, we have also reported on a deeper nitrogen bound exciton center originating most likely from a three nitrogen cluster.[12]

In previous studies, the X_1 center in GaAs has been attributed to the C_{2v} local symmetry.[15] In this representation, six transitions are allowed by the selection rules, each of them being polarized in x, y, or z direction, which have been schematically shown in the inset of Fig. 3(b). Previous PL studies on single impurity centers have been able to resolve only four transitions due to the arrangement of the nitrogen pair with respect to the detection.[15] The existence of six transitions is further supported by the polarization dependent PL spectra shown in Fig. 3. Figure 3(a) shows a two-dimensional polarization map of the bound exciton transitions at 5 K of an ensemble of pair centers. The six vertical black arrows indicate the polarizations in which the transitions maximize, namely, 45° (0° corresponding to horizontal and 90° to vertical), 135° (four lines), and 45°. In Fig. 3(b), the two crucial polarizations of 45° and 135° are shown with the six vertical arrows indicating the transitions. The polarization dependence observed further supports the arrangement of the nitrogen atoms along the [110] direction. The [001] direction is the growth direction, which is perpendicular to the sample surface, and the sample is cleaved along [110] and $[1\bar{1}0]$ directions. The two cleaved sides correspond to the 0° (vertical) and 90° (horizontal) polarizations in the detection. There are a total of 12 indistinguishable arrangements of the nitrogen atoms in the cluster. Four of them are located in the planes parallel to the surface, and eight in the two planes perpendicular to the surface.

The eight N-pair configurations located in the planes perpendicular to the surface are expected to emit light polarized along 45° and 135°, whereas the pair configurations in the planes parallel to the surface should emit light polarized along 0° and 90°. In the ensemble measurement shown in Fig. 3, some of the transitions are not completely suppressed at the perpendicular polarization, indicating the existence of other polarizations, although it appears that there are preferred orientations for the N pairs. The PL studies on single impurity bound excitons have demonstrated to be a powerful tool in lifting the orientational degeneracy and revealing the arrangement of the nitrogen atoms in the lattice.[14–16] This method was introduced in the previous section and has been used in the present study to identify and examine individual N-pair excitonic centers in GaAs. In Fig. 4, a 5×5 μm^2 PL map is plotted. The PL intensity increases arbitrarily from yellow to blue, showing one nitrogen pair excitonic center in the scanned area. The polarization dependence of the PL originating from this particular center is shown in Fig. 5 and is similar to the center reported in Ref. 15 Four transitions can be observed, which maximize at 90°, 0°, 0°, and 90° as indicated by the vertical black arrows. Due to the orientation of the N pair on the plane parallel to the surface, only four excitonic transitions can be observed.[15] In the C_{2v} point group following the notation introduced in Ref. 20, the exciton states reduce to $\Gamma_6\times\Gamma_8=2\Gamma_1+2\Gamma_2+2\Gamma_3+2\Gamma_4$. The transitions from the Γ_1 ground state to the Γ_3 state are forbidden by the selection rules, leading to six allowed transitions sketched in the inset of Fig. 3(b). Several individual impurity pairs were identified, and resolution limited spatial PL maps

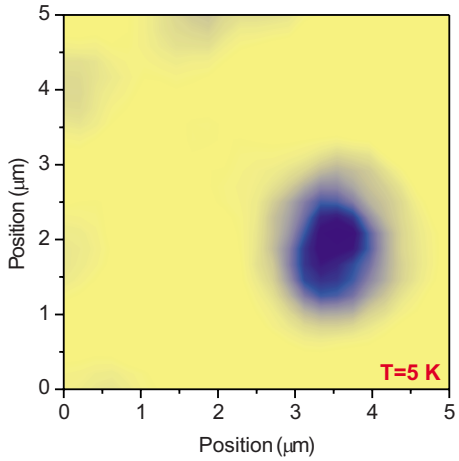

FIG. 4. (Color online) Two-dimensional photoluminescence map of the nitrogen pair bound exciton center at 5 K. In a spacial area of 5×5 μm^2, a single excitonic center has been identified. The polarization map of this center is shown in Fig. 5. The diffraction limited spatial resolution is 0.6 μm^2, and the area was scanned in 0.2 μm steps. The color PL intensity in arbitrary units increases from yellow (light gray) to blue (dark gray).

as the one shown in Fig. 4 were collected. The PL data for one of the identified centers is shown in Fig. 6, where six transitions can be observed. This center is most likely oriented in the planes perpendicular to the surface, showing transitions polarized along −45° and 45°. The fact that such transitions were not observed in the earlier study may be simply due to statistical coincidence.[15] Our observation supports the conclusions of Ref. 15, the C_{2v} center symmetry and the existence of more than four previously observed

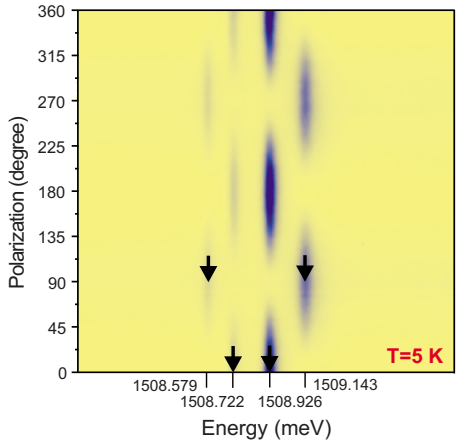

FIG. 5. (Color online) Two-dimensional map of the polarization dependence of a single nitrogen pair bound exciton (X_1) photoluminescence transition at 5 K. The center lies most likely in the plane parallel to the surface. The color PL intensity in arbitrary units increases from yellow (light gray) to blue (dark gray). The four vertical black arrows at 90°, 0°, 0°, and 90° indicate four polarizations at which the transitions maximize. The number of the allowed transitions and the polarization behavior of the emitted light are determined by the symmetry of the center, i.e., the arrangement of the nitrogen atoms in the host lattice.

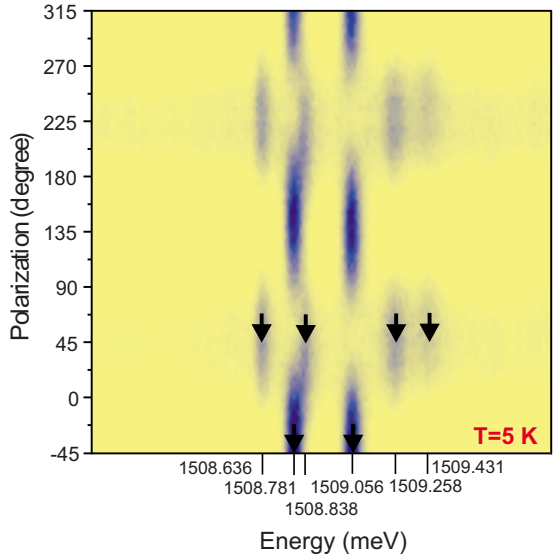

FIG. 6. (Color online) Two-dimensional map of the polarization dependence of a single nitrogen pair bound exciton (X_1) photoluminescence transition at 5 K. The center lies most likely in the plane perpendicular to the surface. The color PL intensity in arbitrary units increases from yellow (light gray) to blue (dark gray). The six vertical black arrows at 45°, −45°, 45°, −45°, 45°, and 45° indicate six polarizations at which the transitions maximize. The number of the allowed transitions and the polarization behavior of the emitted light are determined by the symmetry of the center, i.e., the arrangement of the nitrogen atoms in the host lattice.

transitions. The relative intensities and order of the transitions may be altered by the local environment around this particular N impurity pair. However, the superposition of a large number of single impurity polarization dependent spectra, such as those shown in Figs. 5 and 6, would lead to the ensemble polarization dependence observed in Fig. 3.

In conclusion, high resolution PL spectroscopy was combined with single impurity spectroscopy on high quality N doped GaAs samples in order to study the PL spectra of excitons bound to N impurity pairs. The high spectral resolution spectroscopy resolved a total of six transitions, including transitions which had not been observed in Ref. 15. The photoluminescence lines showed polarization dependent intensity that is similar to the spectral structure and polarization dependence observed in individual N-pair centers. Both techniques support the C_{2v} center symmetry. The comparison between the PL spectra from an ensemble of N pairs and individual centers demonstrates the ability of the latter technique to lift the orientational degeneracy.

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