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Experimental evidence for N-induced strong coupling of host conduction band states in GaN_xP_{1-x}: Insight into the dominant mechanism for giant band-gap bowing

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Direct evidence for N-induced strong coupling of host conduction band (CB) states in GaN_xP_{1-x} is provided by photoluminescence excitation. It is manifested as: (1) a drastic change in the ratio of oscillator strengths between the optical transitions involving the CB minimum (CBM) and the high-lying Γ CB state; (2) a strong blueshift of the Γ CB state with increasing x accompanying a redshift of the CBM, (3) pinning of the localized N states and a newly emerging t_2 (L or X_3) CB state. These findings shed new light on the issue of the dominant mechanism responsible for the giant band-gap bowing of dilute nitrides.

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Dilute nitrides such as anion-mixed $Ga_{1-y}In_yN_xAs_{1-x}$ and GaN_xP_{1-x} alloys represent a new class of highly mismatched semiconductor alloys, which have recently attracted great attention (Refs. 1 and 2 and references therein). Due to strong disparity in electronegativity and atomic size between N and the replaced anion atom, dilute nitrides exhibit many unusual and fascinating physical properties. Among them the most prominent fingerprint is the giant bowing in the band-gap energy. Though it has long been accepted that this giant band-gap bowing is predominantly due to the downshift of the conduction band minimum (CBM), the exact physical mechanism for the CBM downshift remains controversial and has been a subject of intense debate for the last few years. Many proposals have been put forward, which can be summarized into the following three main models: (1) impurity band formation;[3,4] (2) band anticrossing (BAC);[5–7] (3) a polymorphous alloy model.[8,9] The subtle distinction between the three models lies in the evolution of the localized N states and the host CB states in the alloys. The impurity band model argues that the CBM evolves from interacting N-related impurity states (isolated N centers, N pairs and clusters) and requires no participation of high lying host CB states.[3,4] The BAC model includes a mutual repulsion between the N level and the Γ CB state.[5–7] N-induced perturbed host states (PHS) in the third model,[8,9] on the contrary, in principle covers all host CB states that are affected by the perturbation induced by N. The N cluster states (CS), on the other hand, are pinned in energy. Therefore convincing experimental evidence that can reveal the evolution of both N-related localized states and the host CB states with increasing x are required in order to determine the exact physical mechanism responsible for the giant band-gap bowing in dilute nitrides.

The aim of this work is to gain access to the host CB states as well as the localized N states of GaN_xP_{1-x} by employing photoluminescence excitation (PLE) spectroscopy. The GaN_xP_{1-x} alloy was chosen in this study for the following reasons. First of all, this alloy undergoes a band crossover from an indirect band gap to a direct one with increasing x.[6,10] This should give rise to a significant change of the character of the CBM state, which can be more easily detected experimentally. Second, even when the N-related impurity states[11] gradually one by one become resonant with the CB due to the downshift of CBM with increasing x[4,12] they can still be visible in the PLE experiments thanks to a relatively weak oscillator strength of the overlapping band-to-band optical transition at small N compositions. PLE has in the past been shown to be a powerful technique to simultaneously study optical transitions across both direct and indirect band gaps involving various critical points of the fundamental band structure of semiconductors as well as detailed electronic structure of impurities.[13] Reliable optical absorption measurements of thin GaNP epilayers (usually less than 1 μm thick) are challenging because they require removal of the GaP substrate, and the resulting free-standing GaNP film is mechanically weak. Photoreflectance was found to be insensitive to the localized N states and unable to follow simultaneously the evolution of both CBM and highly lying CB states.[6] Though spectroscopic ellipsometry was found to be useful in revealing high-energy critical points in GaNP, it completely failed to detect the CBM state and localized N states.[14]

By employing PLE spectroscopy, we are able to directly and simultaneously monitor the evolution of both localized N states and the host CB states in GaNP. Our new findings provide direct experimental evidence for N-induced strong coupling between the Γ and X host CB states and for pinning of energies of the t_2 (L or X_3) CB state and localized N states. They shed new light on the dominant mechanism for the giant band-gap bowing of the alloy, and also provide a critical test of the validity of various physical models proposed.

The GaNP epilayers (with a thickness of 0.25–0.75 μm) studied in this work were grown by gas-source molecular beam epitaxy on (100) GaP substrates. PLE was performed at 2 K. The tunable light sources used were a xenon lamp fitted with a grating monochromator for a wide spectral range and a dye laser for high-resolution studies over a nar-

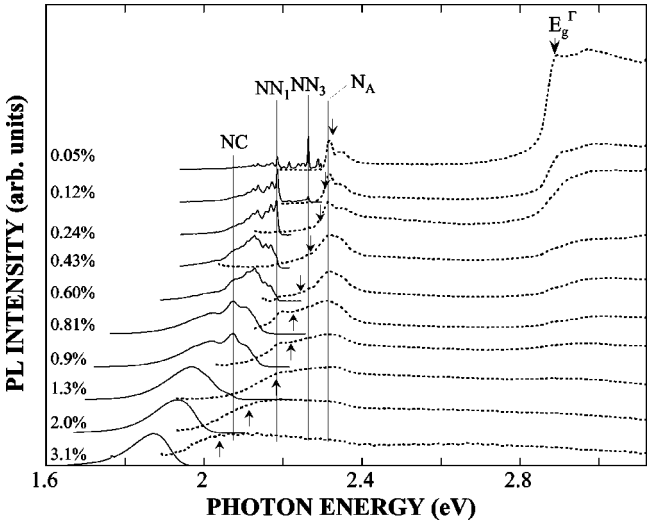

FIG. 1. PL (solid curves) and PLE (dashed curves) spectra measured at 2 K from GaNP with the specified N compositions. The dominant excitonic transitions at the N-related defects are denoted as N_A, NN_3, NN_1 and NC. E_g^Γ indicates the excitonic transition arising from the direct band gap $\Gamma_{15}^v - \Gamma_1^c$. The arrows indicate the alloy band-gap energy determined from independent optical absorption measurements given in Ref. 17. The PL spectra are normalized to their peak intensity, whereas the PLE spectra are normalized to the maximum intensity for photon energy lower than 2.4 eV. The PLE spectra were obtained by monitoring photon energies at 2.102 eV for $0.05\% \leqslant x \leqslant 0.81\%$, at 1.908 eV for $0.9\% \leqslant x \leqslant 2.0\%$, and at 1.851 eV for $x > 2\%$. Both PL and PLE spectra are vertically shifted with each composition for clarity.

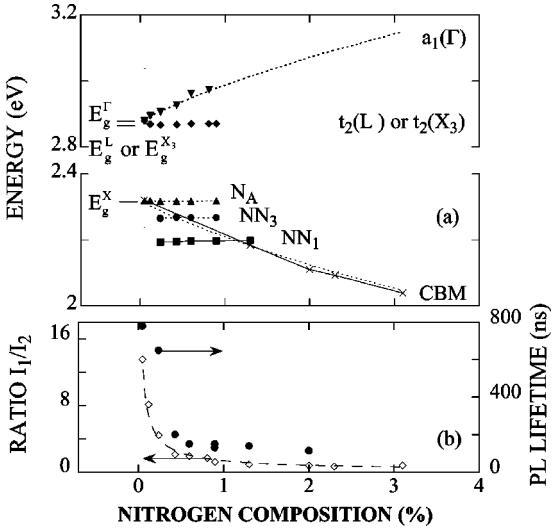

FIG. 2. (a) The experimentally determined energy positions of the N-related PL emissions and the band-to-band transitions between the VBM and the perturbed host CB states, as a function of N composition in GaNP. The crosses and solid line represent the band-gap energy deduced from the optical absorption measurements. The dotted lines are obtained from the best fit of Eq. (1) following the BAC model, with the fitting parameters given in the text. (b) The open diamonds denote the ratio of the PLE intensities (a measure of oscillator strengths) between E_g^Γ and that related to the CBM state. I_2 and I_1 were measured with the excitation photon energies at 2.6 eV (within the continuum derived from the CBM state) and at resonance with E_g^Γ [i.e., the $a_1(\Gamma)$ state], respectively. The closed circles are measured PL lifetimes of the N-related centers in GaNP, after Ref. 10.

row spectral range near the $\Gamma_{15}^v - \Gamma_1^c$ excitonic transition (denoted below as E_g^Γ).[15] The resulting PL was detected by a GaAs photomultiplier after passing through a double grating monochromator.

The solid and dashed curves in Fig. 1 display typical low-temperature PL and PLE spectra,[16] respectively, from the GaN_xP_{1-x} alloys with the specified N compositions. A number of well-known excitonic transitions at the N-related impurity centers such as N_A, NN_3, NN_1 and NC can clearly be seen in the PL or/and PLE spectra.[4,11] The PL emissions disappear one by one starting from the highest energy side as the band gap of the alloy moves down with increasing x, leading to an overall redshift of the PL emissions. The CBM undergoes a significant downshift, apparent from the redshift of the onset of the PLE spectra. More accurate values of the alloy band-gap energy were determined from independent optical absorption measurements,[17] indicated by the arrows in Fig. 1 and the crosses in Fig. 2(a). The PLE features appeared at energies lower than the band gap arise from the localized N states, which can efficiently excite the deeper N states via the well-known excitation transfer process between the N centers.[18] In contrast to the downshift of the CBM, the N-related levels are pinned in energy as observed both in PL or/and PLE [also shown in Figs. 3(a) and 2(a)]. This is true even when the N-related localized levels become resonant with the CB continuum, which rules out the possibility that the CBM is derived from these localized states. Moreover, the ratio of the PLE intensity (a measure of oscillator strengths) between the optical transition near E_g^Γ and that within the continuum derived from the CBM state (e.g., at 2.6 eV where contributions from localized N states are negligible) displays a drastic decrease with increasing x [shown in Figs. 1 and 2(b)], in particular over the N composition range around 0.5% where the band crossover from an indirect to direct band gap takes place.[6,10] This is a direct consequence of N-induced strong coupling between the two CB states involved, such that the CBM state gains significantly the Γ character (thus leading to a quasi-direct band gap) at the cost of the formal Γ CB state. This is further supported by the observed shortening of the lifetime of the excitons bound at the N-related centers (with energy levels still within the band gap) over the same composition range [Fig. 2b],[10] as it is a sensitive function of the character of the nearest CBM state.

In order to obtain reliable information on a possible shift of E_g^Γ, a tunable dye laser was employed in PLE. The resulting PLE spectra are shown in Fig. 3(b). In the GaN_xP_{1-x} alloy with the smallest x (0.05%), two spectral features are seen, i.e., E_g^Γ and $E_g^\Gamma + \Delta$. The latter originates from the optical transition between the spin-orbit split off valence band (VB) state and the Γ CB state, and is generally much weaker and broader, as seen in GaP.[19] Δ is estimated to be about 80 meV, in good agreement with the value reported for GaP in the literature.[19] With increasing x, the E_g^Γ feature evolves

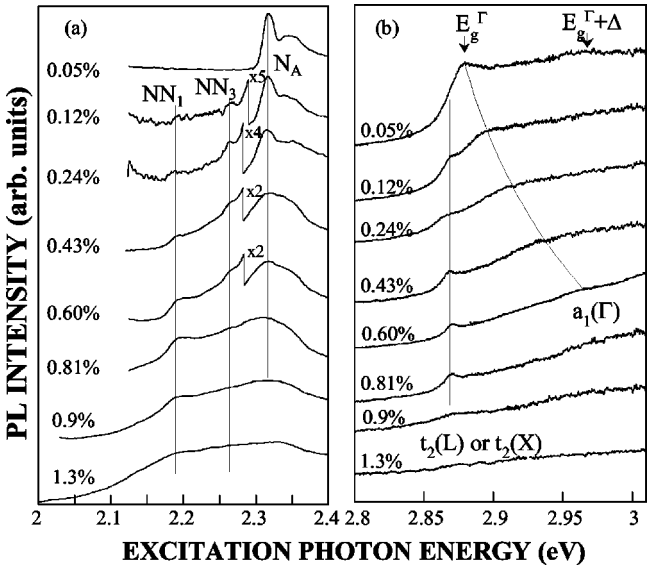

FIG. 3. Evolution of PLE spectra near (a) localized N states and (b) E_g^Γ upon incorporation of N. The lines are guide to the eye. The spectra are shifted vertically for clarity.

into two components. One of them exhibits a clear blueshift and broadening with increasing x, as anticipated by a strong repulsion from the CBM that undergoes a redshift of a similar magnitude as discussed above. The x dependence of E_g^Γ can be approximately described by a linear relation for $x<1\%$: $E_g^\Gamma\ (a_1(\Gamma))=2.876\ \mathrm{eV}+12.756x\ (\mathrm{eV})$. The energy position of the other line is pinned at about 2.870 eV, however, which is nearly independent of x. As the Γ CB state [i.e., $a_1(\Gamma)$] is non-degenerate except for the spin degeneracy, which is not expected to split under the circumstances, the only possible energy splitting of the E_g^Γ transition can occur when the strain field introduced by the lattice mismatch between GaNP and the GaP substrate causes a splitting of the heavy-hole (hh) and light-hole (lh) states at the VB maximum (VBM). The estimated hh–lh splitting from the deformation-potential theory is, however, about one order of magnitude too small[14,20] to account for the observed separation between the two split lines. Therefore another CB state of different origin than the Γ CB state should be involved. Previous studies of the critical points of the fundamental band structure of GaP have indicated that the L and X_3 CB states lie near the Γ state in energy.[13,19] Under the influence of N incorporation, the fourfold-degenerate L valleys can break into the $a_1(L)+t_2(L)$ states, and the X_3 state gives a $t_2(X_3)$ representation.[9] Whereas an a_1 state is expected to be strongly perturbed by the N state of the same symmetry $[a_1(N)]$, a t_2 state should be unperturbed. Therefore we suggest that the new PLE feature pinned at 2.870 eV arises from the optical transition between VBM and $t_2(L)$ or $t_2(X_3)$. The appearance of this line only in GaNP can be attributed to relaxation of the selection rule for this formally forbidden optical transition as a result of N perturbation and alloy effect, and also to the absence of strong spectral overlap with the dominant E_g^Γ as the latter is blueshifted. Due to the weak and broad nature of the $E_g^\Gamma+\Delta$ feature, a similar study of the line splitting and shifting was unfortunately not possible. For the same reason a possible presence and shift of the $a_1(L)$ state could not be determined.

Our results thus clearly show that the CBM cannot be derived from the localized N states judging from the pinning of their energy with increasing N composition. Our new findings of a strong repulsion between the CBM and the Γ CB states and a strong mixing of their X and Γ characters, as well as the pinning of the $t_2(L)$ or $t_2(X_3)$ CB state, give compelling evidence for the N-induced strong coupling of selective host CB states as the dominant physical mechanism for the giant band-gap bowing in GaNP.

Let us now discuss what insight our new findings can provide into the controversy over the physical models proposed for the band-gap bowing in GaN_xP_{1-x}. Let us start with the model of impurity band formation.[3,4] The model was based on the observation of the broadening of the N-related PL lines, e.g., NN_1, already at $x=0.24\%$. Judging from the radius (only 6.4 Å) of the electron localization at the NN_1 center, a critical N doping level about 5.6% is required to ensure significant wave function overlap needed for impurity band formation.[4] Experimentally, however, a significant band-gap reduction was already observed at $x<1\%$. To explain this, an excitonic effect was proposed involving a larger radius (16 Å) of the loosely bound hole of a bound exciton at the N centers. The critical N doping level is in this case estimated to be about 1.4%.[4] We can safely rule out this model as being the origin of the band-gap bowing for the following reasons. First, the maximum density of the photogenerated excitons under our experimental PLE condition with a xenon lamp as the light source, assuming 100% conversion efficiency and an exciton lifetime of 1 μs, is estimated to be three orders of magnitude lower than the required critical level of 1.4% for the exciton mediated impurity band formation. Nevertheless the band-gap bowing is clearly seen under our experimental condition. Second, the impurity band formation is not expected to affect the high lying host CB states. This is again in contradiction to our experimental finding of the blueshift and splitting of the CB states near E_g^Γ. It should be pointed out that inhomogeneous alloy broadening of the N-related levels has been commonly observed in conventional AlGaAs and GaPAs alloys,[21,22] which can also occur in GaNP explaining at least partially the observed broadening of the N-related excitonic PL lines. Other possible contributions to the line broadening can be strong interactions with host CB states and lifetime effects.

Now let us turn to the BAC model. According to this model, the interaction of the localized N states and the extended Γ CB state of the GaP matrix splits the CB into two subbands, with their energies following[5–7]

$$E_\pm(k)=\frac{1}{2}[(E_{M\Gamma}(k)+E_N)\pm\sqrt{(E_{M\Gamma}(k)-E_N)^2+4xC_{NM}^2}]. \tag{1}$$

Here $E_{M\Gamma}(k)$ is the dispersion relation at the Γ CB edge, E_N is the energy of the localized state derived from the substitutional N atoms, x is the N fraction, and C_{NM} is the coupling parameter depending on the semiconductor matrix. The band-gap energy is given by the energy of the lower subband

edge, $E_-(0)$, relative to the VBM. In the case of GaNP, $E_-(0)$ should originate from the localized N states E_N. The results from a best fit of Eq. (1) to the values of E_g^Γ and CBM obtained in this work at 2 K is shown as dotted lines in Fig. 2(a), yielding $E_{M\Gamma}(0)=2.88$ eV, $E_N=2.32$ eV, and $C_{NM}=2.7$ eV. The agreement is rather good, which makes it tempting to suggest that the BAC model provides a correct description. However, the experimental fact that the energy positions of the N-related levels do not change with x [Figs. 1, 2(a) and 3(a)] contradicts with what is expected by the BAC model, and thus seems to make it unfavorable. Nevertheless, the BAC model seems to be able to provide a rather satisfactory phenomenological description of the observed shifts of the CBM and Γ CB state.

In the polymorphous alloy model, the multiband empirical pseudopotential method and atomically relaxed large supercells were used to study the evolution of the electronic structure of GaN_xP_{1-x}.[9] It is the interactions between N-induced localized CS and many PHS of the underlying host GaP that determines the electronic band structure of the GaNP alloy. As x increases, the energy of the CS is pinned while the energy of the lowest PHS plunges down due to the level repulsion from the other upper lying interacting PHS, thereby overtaking the CS and forming the new CBM. This is qualitatively in good agreement with our experimental observations, shown in Figs. 1 and 2(a). The predicted increasing Γ character of the CBM with increasing x also supports the increasing optical transition probability of the CBM state observed in our experiments [Fig. 2(b)]. A selective coupling between all a_1-like host CB states [i.e., $a_1(X_1)$, $a_1(L)$, $a_1(\Gamma)$] by $a_1(N)$ can explain the observed large blueshift of $a_1(\Gamma)$, the redshift of the CBM, and the pinning of $t_2(L)$ [or $t_2(X_3)$]. Unfortunately, quantitative theoretical predictions of evolution of CB states by empirical pseudopotential method are not available to date and it is therefore unclear if the theoretical model can provide satisfactory quantitative agreement with our experimental results.

In summary, the following experimental facts have been established for GaNP from this work: (1) a drastic change in the ratio of oscillator strengths between the optical transition near E_g^Γ and that near the CBM; (2) a strong blueshift of the $a_1(\Gamma)$ PHS with increasing N composition accompanying a redshift of the CBM; (3) pinning of the energies of the N-related levels; (4) appearance of the $t_2(L)$ or $t_2(X_3)$ upon N incorporation, of which the energy position is insensitive to N composition. Our findings provide direct experimental evidence for N-induced strong coupling of symmetry-allowed host CB states and their level repulsion as the dominant mechanism for the giant band-gap bowing in GaNP, calling for further theoretical studies.

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