Confirmation of the impurity-band model for GaP$_{1-x}$N$_x$

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Low-temperature absorption studies on freestanding GaP$_{1-x}$N$_x$ films provide direct experimental evidence that the host conduction band minimum (CBM) near X_{1C} does not plunge downward with increased nitrogen doping contrary to what has been suggested recently, but in fact remains stationary for x up to 0.1%. This, combined with the results of earlier studies of the CBM at Γ and conduction band edge near L, confirms that the giant band-gap lowering observed in GaP$_{1-x}$N$_x$ results from a CBM that evolves purely from nitrogen impurity bands.

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The giant band-gap lowering observed in the dilute nitride alloys GaAs$_{1-x}$N$_x$ and GaP$_{1-x}$N$_x$ has made them the subject of several recent experimental and theoretical investigations, because they show promise for use as solar cell and semiconductor diode laser materials.[1–5] However, despite almost a decade of effort, this promise remains yet to be fulfilled, because the anomalously large band-gap bowing in these materials occurs concomitantly with several inherent abnormal alloy properties such as poor electron mobility and minority carrier lifetime.[6] Nitrogen forms a series of isoelectronic trap states in both GaAs and GaP that are associated with either the isolated substitutional impurity, or with substitutional impurity pairs, triplets, and higher-order clusters.[7–9]

A great deal of attention has been focused on the perturbation of the host conduction band minimum (CBM) induced by these nitrogen impurity states in an effort to explain the giant band-gap lowering, and this has led to three distinct models for the origin of this phenomenon.[1,2,4,5,10,11] The first is a two-band model, also known as the band-anticrossing model (BAC).[2,4] This phenomenological model explains the bowing as being a result of repulsion between two levels, the isolated nitrogen impurity level N$_X$ and the CBM Γ_{1C} at the zone center.[2] Here, since the N$_X$ impurity level lies above Γ_{1C} in GaAs, the repulsion causes the host CBM Γ_{1C} to be lowered resulting in the giant bowing.[2] In GaP the N$_X$ level (referred to as the *A* line) lies below Γ_{1C}, and so the situation is reversed with N$_X$ being repelled downward and Γ_{1C} upward.[4] In this case, the N$_X$ level is supposed to evolve into the new CBM. The second model which is based on an empirical pseudopotential band-structure calculation of the alloys and in its later versions also accounts for the effects of nitrogen pairs and clusters, is referred to as the polymorphous model.[5] In this model, for GaAs$_{1-x}$N$_x$, with increasing nitrogen content, the host conduction band direct edge Γ_{1C} plunges downward primarily due to the Γ-L repulsion and overtakes the stationary impurity bound states, hybridizing with them. The same arguments were applied to the host conduction band indirect edge in GaP.[5] Both the first and second models universalize their approach for GaAs$_{1-x}$N$_x$ to GaP$_{1-x}$N$_x$ overlooking the important differences between these two systems. For example, the indirect band gap in GaP with a large density of states at its *X* valley makes a major difference from the direct band gap in GaAs with a small density of states at its Γ valley, when considering the impurity-host interaction and the relative absorption strength between the impuritylike and hostlike states.[11]

The third model which was the first to focus on nitrogen impurity band effects is referred to as the impurity band model.[11] It recognizes the subtle differences between GaAs and GaP and the interplay between level repulsion and impurity band formation in affecting the band-edge absorption. According to this model, N-induced bound states in GaAs$_{1-x}$N$_x$ do form an impurity band but their density of states is too low to lead to a significant absorption compared to that of the hostlike states.[11] Nevertheless, they are sufficiently abundant to cause a significant reduction in the carrier lifetime and diffusion length, and abnormal electronic properties near the absorption tail of the alloy.[6,11] In the third model, for GaP$_{1-x}$N$_x$, the discrete absorption lines in the dilute doping limit broaden and merge into a continuum absorption band with increasing N doping, leading to the redshift of the absorption edge, whereby the CBM of GaP$_{1-x}$N$_x$ is effectively comprised of nitrogen impurity band states. These conclusions were corroborated by resonance Raman studies.[12] In fact, the impurity band model is developed naturally from the earlier studies where the formation of the impurity band of isolated N centers[13] and the formation of the triplet N centers[14] have been discussed theoretically, and these effects have been shown to manifest either as a broadening of the *A* line in absorption or the additional emission on the lower energy side of NN$_i$ peak.[15] However, recent experimental and theoretical studies have claimed to provide evidence that this is untrue and that the giant lowering of the band gap in GaP$_{1-x}$N$_x$ is indeed caused by the host CBM plunging downward with increased nitrogen doping.[16,17] Using low-temperature absorption studies on a set of carefully prepared GaP$_{1-x}$N$_x$ samples, we now present direct experimental evidence for the contrary.

In order to probe the indirect (*X*) and direct (Γ) band gaps, optical absorption was measured on 2-μm-thick, metal-organic chemical vapor deposition (MOCVD) grown GaP$_{1-x}$N$_x$ epilayers that had been removed from their GaP substrates. For measurements near the indirect excitonic gap E_{gx}, additional samples approximately 100 μm thick grown by liquid phase epitaxy (LPE) were also utilized.[18] The growth and characterization of the MOCVD and LPE samples are described in Refs. 12 and 18, respectively. The epilayers were held freestanding in He vapor at 1.6 K, oriented at Brewster's angle with the light from a tungsten-halogen lamp. For the sensitive measurement of E_{gx}, the epi-
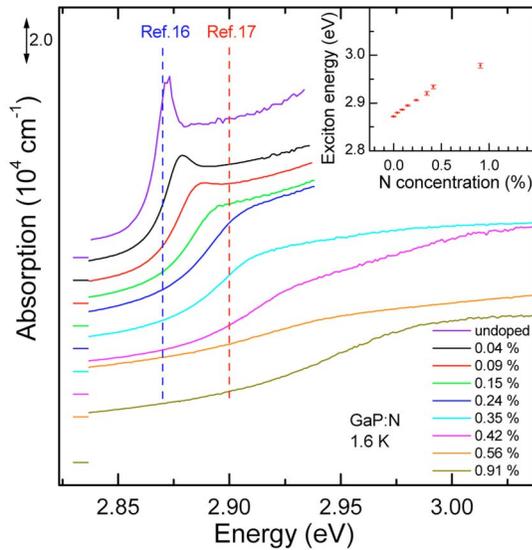
FIG. 1. (Color online) Low-temperature absorption in the GaP:N direct band-gap spectral region for increasing nitrogen concentration. Curves are displaced vertically for clarity as shown by the zero levels at the left. Vertical lines indicate energies of the proposed t_2 transition (2.870 eV) measured in PLE (Ref. 16) and the localized cluster states of single N atoms (2.90 eV, Ref. 17). Inset: energy of the excitonic band gap, $E_{g\Gamma}$, as a function of nitrogen concentration, obtained by fitting the absorption to a Gaussian exciton peak and a broadened continuum edge. The error bars represent fitting uncertainty. No fitting was attempted on the 0.56% sample.

layer thickness was increased up to 10 μm, and multiple epilayers were stacked to increase the transmission length.

Figure 1 shows low-temperature absorption spectra measured near the Γ_{1C} direct excitonic band edge for free standing GaP$_{1-x}$N$_x$ epilayers. The strong excitonic absorption feature observed in the more lightly doped samples is indicative of their high electronic quality that is not degraded by the lift-off process. The two vertical dashed lines in Fig. 1 denote the expected positions of a new spectral feature that remains stationary with increasing x, observed in Ref. 16 and predicted in Ref. 17. The absence of the feature in spectra from our lifted-off samples suggests that this feature observed previously in Ref. 16 in photoluminescence excitation spectroscopy (PLE) was perhaps associated with the GaP buffer layer. With increasing N, the blueshifting of the Γ_{1C} band edge (inset of Fig. 1), previously noted in spectroscopic ellipsometry studies,[19] is now unambiguously confirmed in Fig. 1. The BAC model interprets this blueshift as resulting from the repulsion between Γ_{1C} and N$_X$.[4] There the redshift of the low-temperature photoluminescence (PL) peak in GaP$_{1-x}$N$_x$ is attributed to the redshift of N$_X$.[4] However, several studies using low-temperature absorption and PLE studies have concluded that the A line (N$_X$ level) remains stationary with increasing N content, questioning the validity of the BAC model for GaP$_{1-x}$N$_x$.[10,16,20] Recently, Buyanova et al. made a claim for the redshift of the GaP$_{1-x}$N$_x$ indirect CBM, based on their determination of the band-gap energy from fitting their absorption and PLE spectra.[16] But it was pointed

out by Zhang et al. that since the N-induced bound states (a hierarchy of impurity complexes) give rise to rather strong absorption below the indirect band gap, the position of the absorption edge cannot be defined in a conventional way for GaP$_{1-x}$N$_x$.[10,11] They showed that the relative intensity of the more distant nitrogen impurity pairs relative to the A line increases with increasing nitrogen doping and that the absorption between the main absorption peaks in fact comes from either excited states or phonon side bands for the low nitrogen content samples, with added contribution from the line broadening effects in the high nitrogen content samples.[21,22] However, as is evident from the recent work in Refs. 16 and 17, this interpretation has remained contentious because of the difficulty in directly ascertaining the location of the host CBM near X_{1C}.

Therefore, we have now performed a very precise study of the optical absorption in the vicinity of the indirect gap in dilute GaP$_{1-x}$N$_x$, where the evolution of the host states can be observed free from overlapping impurity absorption. In this dilute regime, the effect of the nitrogen impurity-induced perturbation on the host CBM near X_{1C} causes a weak feature referred to as the A_X line that is attributed to the threshold of the indirect free-exciton energy gap, E_{gx} to become observable in the low-temperature absorption spectrum.[7,23,24] This feature can be used as a marker for the position of the indirect gap near X_{1C} for dilute N samples as shown in the lower spectra of Fig. 2. The upper spectra track this gap energy as nitrogen is increased. The free-exciton feature that is broadened as a result of scattering from nitrogen impurities gets smeared out for concentrations beyond those shown. Figure 3 shows the variation of A_X with N composition in the range from 0.008% to 0.1%. The inset of Fig. 3 contrasts this variation with the variation of the band gap estimated in Ref. 16 for this region. Evidently, in the 0.008% to 0.1% N composition range, A_X and, therefore the host indirect CBM near X_{1C}, remains practically stationary, with no evidence of the host CBM plunging down, which, being a symmetry-induced effect, should definitely have turned on in the very dilute range investigated. In fact, judging from the results for GaAs$_{1-x}$N$_x$,[25–27] where the repulsion turns on for x well below 0.001%, is linear up to $\approx$1%, and only saturates at high nitrogen concentration,[28] were there to be any shift in the 0.008% to 0.1% composition range for GaP$_{1-x}$N$_x$, Fig. 3 indicates that it would be two orders of magnitude smaller than that claimed in Ref. 16. A careful examination of the absorption spectra for the more dilute GaP$_{1-x}$N$_x$ samples in Fig. 1 of Ref. 16 reveals the absurdity of attempting to extract the position of the CBM by modeling the absorption onset, because, as is evident, the absorption from the A line becomes increasingly predominant as the nitrogen concentration decreases. In fact, in ultradilute samples, this is the only remaining absorption.

The plunging downward of the CBM near X_{1C} as claimed in Ref. 16, obtained from modeling of their absorption data, was offered by these authors as a corroboration of the predictions of the polymorphous model of Kent et al.[5] Consequently, Dudiy et al. in a refinement of the polymorphous model for GaP$_{1-x}$N$_x$, argued that the $a_1(X_{1C})$ state was located below the $e(X_{1C})$ state (rather than above it, as suggested earlier by Kent et al.) and that this state moving rap-
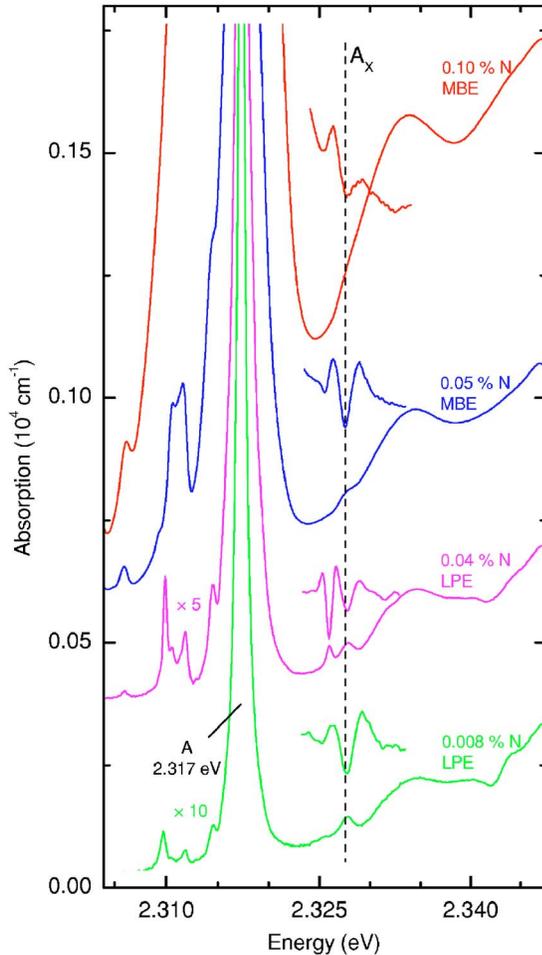
FIG. 2. (Color online) Expanded plot of absorption near the indirect band gap in four thick GaP:N samples. Strong absorption near 2.317 eV is the isolated nitrogen peak and the broad peak near 2.333 eV is associated with its TA sideband. Between these is the indirect band-gap exciton, identified by the A_x peak and marked by the vertical line at 2.3275 eV. Limited range spectra for each sample show the normalized second derivative of absorption used to precisely locate the A_x feature. The total sample thicknesses of 24 μm for 0.05% N and 30 μm for 0.10% N were used.

idly downward with increasing nitrogen doping (as opposed to remaining stationary as suggested by Kent *et al.*) hybridizes with the nitrogen impurity cluster states and forms the new CBM of the alloy, while the $e(X_{1C})$ state remained stationary.[17] Their evaluation of the Γ, X, L character densities revealed that the stationary $e(X_{1C})$ state, which couples very weakly to the cluster states, had negligible Γ character, whereas the downward moving host CBM (low energy of the perturbed host states in Ref. 17) that comprises the $a_1(X_{1C})$ state that hybridizes with the cluster states, had strong Γ character.[17] Thus A_X must be associated with the latter state.

A more careful analysis of the spectra in Fig. 2 performed by taking the second derivative of the spectral region around the A_X feature, reveals the existence of a weak feature roughly 2 meV lower in energy that also remains stationary with nitrogen concentration in the range studied. Since this very weak feature appears unexpectedly stronger than A_X in
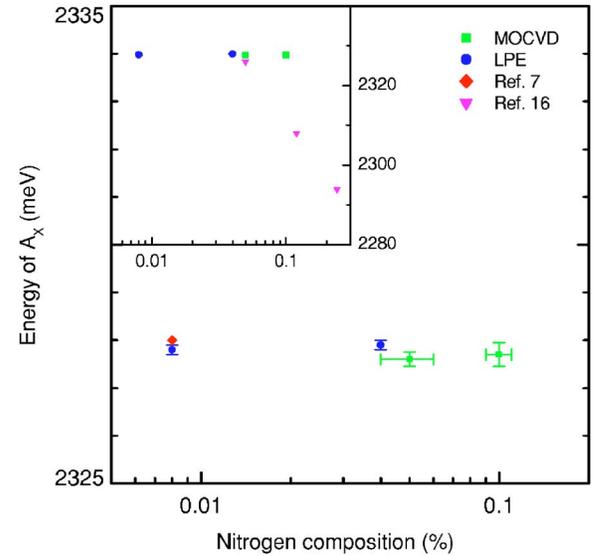
FIG. 3. (Color online) Measurements of the indirect band-gap exciton in Fig. 2 as a function of nitrogen concentration. Squares: MOCVD samples; circles: ≈ 100 μm LPE samples; diamond: samples in Ref. 7 with their low-concentration limit revised using Ref. 24. Inset: The vertical axis is compressed to show the above data in comparison to the alloy band gaps extracted from absorption onset measurements in Ref. 16.

just one sample, at 0.04%, we attribute it to the excited state of sulfur-bound excitons, based on the previous assignment of the same feature denoted as C' in Ref. 23. The data of Fig. 3 show no evidence of the downward repulsion of A_X, and thus are in contradiction with the claims of Refs. 16 and 17 for the rapid downward movement of the host CBM near X_{1C} with increasing N as the reason for the anomalous lowering of the band gap observed for GaP$_{1-x}$N$_x$. However, our data corroborate the conclusions of the resonance Raman studies of Ref. 12 that the host CBM near X_{1C} remains stationary with increasing nitrogen content. Combining these results with the conclusions for increased nitrogen doping from the ellipsometry studies of Ref. 19 and the resonance Raman studies of Ref. 29 that the E_1 transition and hence the conduction band edge at L_{1C} does not move rapidly downward, and with the conclusions of Refs. 16 and 19, and the present work that the CBM at Γ_{1C} does not move rapidly downward, makes it now possible to assert that none of the host CBMs plunge downward with increasing nitrogen doping, and that the CBM in GaP$_{1-x}$N$_x$ evolves purely from nitrogen impurity bands as had been suggested earlier by the resonance Raman studies of Ref. 12. Our results challenge the validity of the BAC and polymorphous models for GaP$_{1-x}$N$_x$, but corroborate the conclusion of Ref. 11 that due to the dissimilarity between GaP$_{1-x}$N$_x$ and GaAs$_{1-x}$N$_x$, seeking a universal model for the band-gap lowering that applies to both the isoelectronic doping systems is unrealistic.

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