

Effect of nitrogen on the electronic band structure of group III-N-V alloys

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We have studied optical transitions at the Γ and L points of the Brillouin zone of $\text{GaN}_x\text{As}_{1-x}$ and $\text{Al}_y\text{Ga}_{1-y}\text{N}_x\text{As}_{1-x}$ alloys using photomodulation spectroscopy. For $\text{GaN}_x\text{As}_{1-x}$ with N contents between 0% and 2%, the N-induced shift of the conduction-band L minima is found to be only a fraction of the conduction-band edge shift at the Γ point. The measurements of $\text{Al}_y\text{Ga}_{1-y}\text{N}_x\text{As}_{1-x}$ further show that there is no correlation between the location of the X conduction-band minima and the observed E_+ and E_- transitions. The results demonstrate that the N-induced interactions between extended Γ , L , and X conduction-band states do not play a significant role in modification of the conduction-band structure of III-N-V alloys. The N-induced change of the conduction-band structure is predominantly influenced by the anticrossing interaction between the extended states of the Γ conduction band and the localized states of nitrogen.

A new class of semiconductor alloys in which one of the constituent elements is replaced by an element with highly dissimilar properties has been discovered recently. These new alloys exhibit a range of unexpected characteristics. It has been found that the substitution of the group V element in group III-V compounds with small amounts of nitrogen leads to dramatic changes of the electronic properties.¹⁻⁵ The most important effect is a large reduction of the fundamental band gap. For example, a 0.18 eV reduction of the band gap has been observed in $\text{GaN}_x\text{As}_{1-x}$ at $x = 0.01$.⁵

A major advancement in the understanding of the effects of nitrogen on the electronic structure of III-N-V alloys was recently achieved with the observation of an additional, high-energy E_+ edge in the optical transitions.^{6,7} The appearance of the E_+ edge, as well as its alloy composition and pressure dependencies, have been explained in terms of an anticrossing interaction between localized N states and the extended Γ states of the conduction band of the host semiconductor matrix.^{6,8} The interaction splits the conduction band into two subbands (E_- and E_+). The downward shift of the lower E_- subband is responsible for the reduction of the fundamental band gap, and the transitions to the upper E_+ subband account for the high-energy edge. The model has been successfully used to describe quantitatively the dependencies of the upper and lower subband edges on the hydrostatic pressure and N content.⁸ Further justification for the band anticrossing model has been provided recently within a tight-binding approach.^{9,10}

Alternative interpretations of some of the observed effects have been proposed recently.^{11,12} The new proposals are based on band-structure calculations using the density-

functional theory with the local density approximation (LDA) (Ref. 11) and a combination of LDA and the empirical pseudopotential method.¹² Although the results of the calculations given by those two approaches differ significantly, their proponents assert that the observed changes in the conduction-band structure are a result of a nitrogen-induced interaction between states originating from the extended states of the Γ , L , and/or X minima. They argue that since incorporation of N breaks the crystal symmetry, it splits the degenerate L and X minima, resulting in strong interactions of the a_1 symmetry states with the states of the Γ minima. Specifically, Ref. 12 suggests that the observed E_+ transition originates from a configuration-weighted average of a nitrogen-induced resonant impurity state $a_1(\text{N})$ and the $a_1(L_{1C})$ state, and Ref. 11 proposes that the N-induced repulsive interactions between the Γ -like and X -like conduction-band states are responsible for the downward shift and a large nonlinear and reduced pressure dependence of the fundamental band gap.

In order to clarify the importance of these different interactions and to test these models, we have studied the E_1 transition ($\Lambda_{4V,5V} - \Lambda_{6C}$) near the L points of the Brillouin zone, concurrently with the transitions from the valence band to the two conduction subbands (E_- and E_+) at the Γ point, in $\text{GaN}_x\text{As}_{1-x}$ to examine the N-induced change of the L conduction-band edges. N-induced changes in optical transitions in $\text{Ga}_{1-y}\text{Al}_y\text{N}_x\text{As}_{1-x}$ have also been studied. Our results show that the extended L and X conduction-band states do not play any significant role in the observed N-induced modification of the conduction band structure of III-N-V alloys.

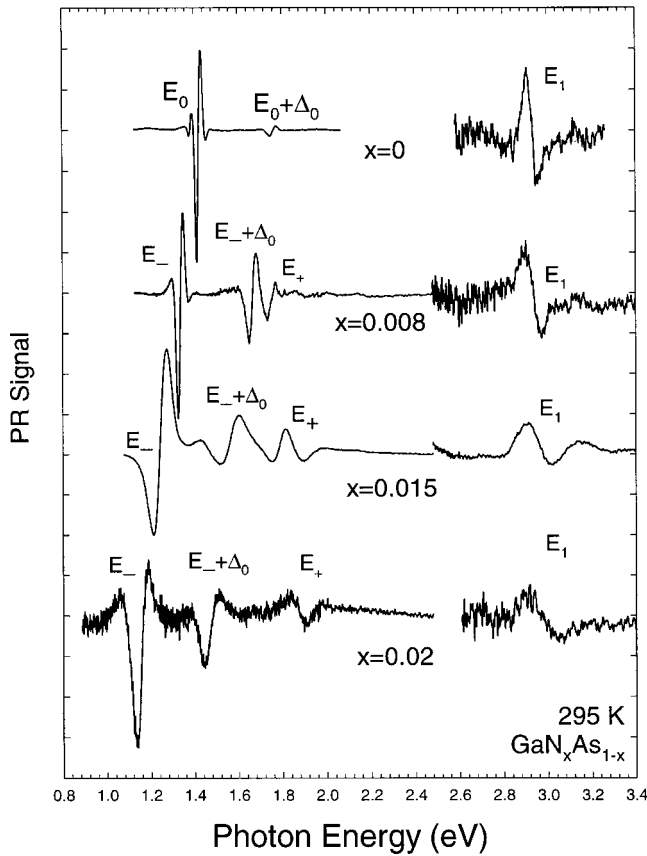


FIG. 1. PR spectra taken from several $\text{GaN}_x\text{As}_{1-x}$ samples at 295 K.

The $\text{GaN}_x\text{As}_{1-x}$ samples used in this study were grown by metal-organic chemical vapor deposition. Details of the growth method were reported elsewhere.¹³ Two $\text{Al}_y\text{Ga}_{1-y}\text{As}$ thin films (with thickness $\sim 0.5 \mu\text{m}$) were grown by metal-organic vapor phase epitaxy on GaAs substrates with ~ 100 – 200 \AA GaAs cap layers on top. The composition of the $\text{Al}_y\text{Ga}_{1-y}\text{As}$ thin films were determined by Rutherford backscattering spectrometry (RBS) to be $y=0.32\pm 0.04$ and 0.63 ± 0.04 . N^+ implantation was carried out at room temperature using multiple energies at 30, 68, and 120 keV with a total dose of 9.3×10^{15} ions/ cm^2 , creating $\sim 2500 \text{ \AA}$ -thick layers with uniform N contents.¹⁴ Secondary-ion-mass spectroscopy measurements showed that the N concentration in the implanted layer is $\sim 3\times 10^{20} \text{ cm}^{-3}$ (corresponding to $\sim 1.3\%$ of the N content). Rapid thermal annealing was performed in a flowing N_2 ambient at 800 – $945 \text{ }^\circ\text{C}$ for 10 sec with the sample surface protected by a GaAs wafer.

Photoreflectance (PR) measurements were performed to measure optical transitions in the samples at room temperature. Quasimonochromatic light from a halogen tungsten lamp dispersed by a 0.5 m monochromator was focused on the samples as a probe beam. A chopped HeCd laser beam (3250 or 4420 \AA) provided the photomodulation. PR signals were detected by a Ge or Si photodiode using a phase-sensitive lockin amplification system.

Shown in Fig. 1 are several PR spectra of $\text{GaN}_x\text{As}_{1-x}$ taken over a wide energy range from 0.8 to 3.5 eV. In the samples with $x>0$, the E_- and E_+ transitions can be clearly observed. The E_- transition corresponds to the fundamental band gap of GaNAs, and the E_+ transition is related to a new

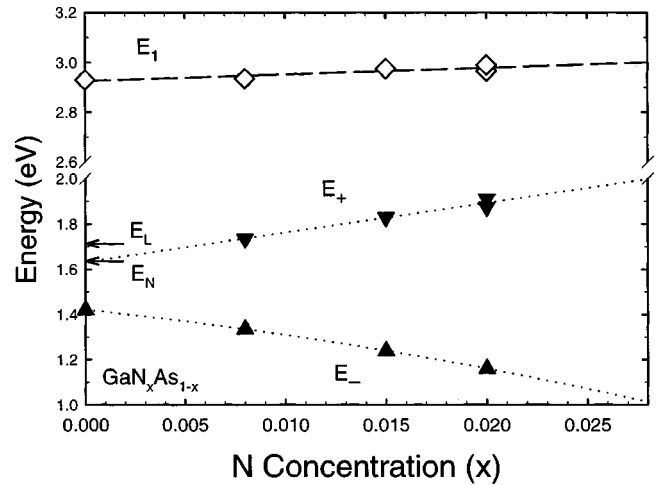


FIG. 2. Change in the energy position of the E_- and E_+ , as well as the E_1 transitions as a function of N concentration. The arrows mark the energy position of E_N and E_L relative to the top of the valence band in GaAs.

and unique conduction-band edge of GaNAs caused by the incorporation of N into GaAs.^{6–8} E_- shifts down and E_+ shifts up with increasing N content. On the higher energy side, the spectral feature associated with the E_1 transition from the $L_{4,5}$ valence-band edge to the L_6 minima of the conduction band can be also clearly observed in all the samples. The change of E_1 transition energy, as well as the shifts of E_- and E_+ transitions, is plotted in Fig. 2 as a function of the N concentration in $\text{Ga}_x\text{N}_{1-x}\text{As}$. The transition energies were determined by fitting PR spectral features to the line shape functional form of three-dimensional interband transition.¹⁵

It is clear from Fig. 2 that within the experimental uncertainties the relative energy shift of the E_+ transition as a function of N concentration is exactly the same as that of the fundamental band gap in the $\text{Ga}_x\text{N}_{1-x}\text{As}$ samples represented by a downward shift of the E_- transition. The appearance of the E_+ transition and its composition dependence have been explained by a two-level anticrossing interaction, where the upward shift of the upper state and the downward shift of the lower state are exactly the same and equal to $[(E_a - E_b)^2 + 4V^2]^{1/2} - |E_a - E_b|/2$, where E_a and E_b are the original energy levels, respectively, and V is the parameter describing the strength of the interaction.^{6,8} In the case of $\text{Ga}_x\text{N}_{1-x}\text{As}$, these two interacting levels are the electronic state of nitrogen (E_N) and the bottom of the conduction band (E_M) of GaAs, and $V = C_{NM}x^{1/2}$ with $C_{NM} \approx 2.7 \text{ eV}$. The fundamental band edge (E_-) and the E_+ edge are related through the anticrossing interaction of the N level with the Γ conduction-band edge of the GaAs. The states of the E_- and E_+ subbands are represented by wave functions that are a mixture of extended conduction-band and localized nitrogen states. Extrapolating the experimental data of E_+ shown in Fig. 2 to GaAs yields $E_N = E_V + 1.64 \pm 0.01 \text{ eV}$ for nitrogen impurity ($x \rightarrow 0$). This is in excellent agreement with the values observed in N doped GaAs.^{16,17} In fact, the N level was found to be independent of the nitrogen concentrations up to $1\times 10^{20} \text{ cm}^{-3}$ in GaP (Ref. 18) and $x=0.21\%$ in GaAs.¹⁹ It is important to note that, as more and more nitrogen atoms are incorporated into GaAs to form the GaNAs

alloy, the wave functions of extended conduction-band states and localized nitrogen states mix together, leading to the evolution of the nonparabolic E_- and E_+ subbands. Isolated N states with a highly localized impurity character no longer exist in the alloys.

Recently, the close proximity of the L minimum energy at $E_L = E_V + 1.705$ eV to the energy of the localized N state in GaAs has been invoked in the argument that interaction of these states could induce a disorder-activated $\Gamma_V - L_C$ transition responsible for the E_+ transition.⁷ The observation of the E_1 transition shifting toward higher energies at a much slower rate ($\sim 20\%$) compared to the E_+ transition rules out the possibility that the E_+ transition results from an N-induced $\Gamma_V - L_C$ transition. The slow, monotonic increase of the E_1 transition energy with N concentration is also contrary to the theoretical prediction that the observed E_+ transition originates from a configuration-weighted average of a mostly nitrogenlike $a_1(N)$ level and an $a_1(L_C)$ level split from the L conduction-band edge due to the incorporation of N into GaAs. The theory predicts a N-induced splitting of the L conduction-band edge into two levels (a_1 and t_2), and the lower $a_1(L_C)$ level has a large downward shift with N content.¹² Should that occur, one would expect to observe a decrease of the E_1 transition energy as a result of the downward shift of the lower $a_1(L_C)$ level, rather than an increase in energy with respect to that of GaAs at 2.925 eV. Moreover, a splitting of the L -band edge will result in observing a different PR spectral line shape of the E_1 transition in $\text{Ga}_x\text{N}_{1-x}\text{As}$ from that in GaAs. The sensitivity and spectral resolution of the PR experimental technique used in this work are high enough to detect both a_1 and t_2 transitions. However, as shown in Fig. 1, the PR line shapes associated with the E_1 transition in samples with different N concentrations do not exhibit any significant changes except the gradual broadening primarily caused by the incremental alloy compositions.

It would be tempting to explain the small shift of the E_1 transition by an interaction of L -minimum states with the N states. However, one should keep in mind that alloying of GaAs with GaN leads also to a continuous change of the E_1 energy. Band-structure calculations show that in zinc-blende GaN the E_1 transition is expected to occur at the energy of 5.8 eV.²⁰ A standard interpolation scheme with a small bowing effect can well describe the observed variation of the E_1 energy with alloy composition. The dashed line in Fig. 2 is a least-square fit to the data. The best fit yields $E_1(x) = 2.925 + 2.664x + 0.221x^2$ eV.

In order to demonstrate that the energy position of the E_+ edge is also insensitive to the energy position of the X conduction-band edges of the matrix material, we have studied the effect of N on the band structure of $\text{Al}_y\text{Ga}_{1-y}\text{As}$ alloys. In these alloys the Γ band edge shifts from about 0.5 eV below to slightly more than 0.5 eV above the X band edges. This large relative energy shift should strongly affect the strength of the interaction between those two levels. Positions of the experimentally observed E_+ and E_- transitions for $\text{GaN}_{0.008}\text{As}_{0.992}$ and two $\text{Ga}_{1-y}\text{Al}_y\text{NAs}$ samples are shown in Fig. 3. The well-known dependencies of the Γ , L , and X conduction-band minima on the Al content are also shown in the figure. The composition of the $\text{Ga}_{1-y}\text{Al}_y\text{As}$ wafers was accurately determined from the measured posi-

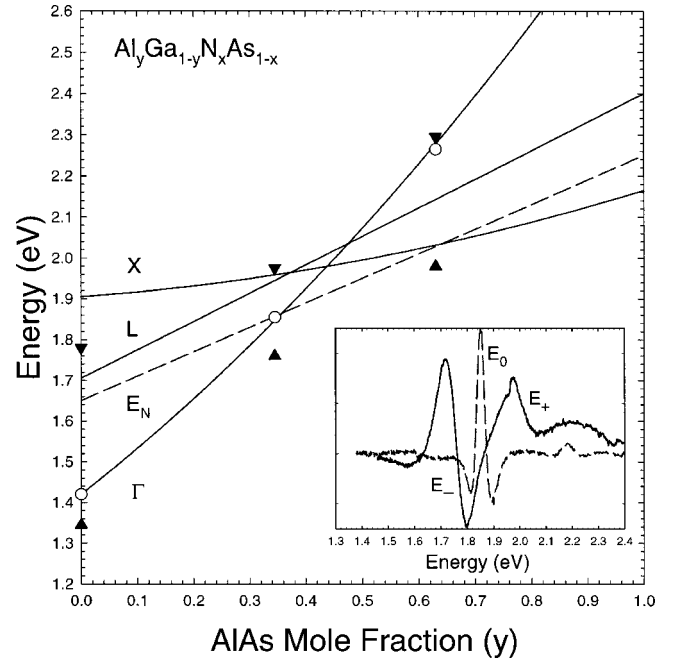


FIG. 3. The E_- and E_+ transition energy (triangles) measured for $\text{Al}_x\text{Ga}_{1-x}\text{NAs}$ samples. The open circles represent E_0 transitions in samples with no nitrogen. The variation of the Γ , X , and L conduction-band edges as a function of the AlAs mole fraction in $\text{Al}_y\text{Ga}_{1-y}\text{As}$ alloys are shown by the solid lines. The dashed line represents the change of the E_N position with Al content. The inset shows the PR spectra measured on the $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ samples with (solid line) and without (dashed line) N.

tion of the E_0 transition in the as-grown wafers. The values of $y=0.35$ and 0.64 are in reasonably good agreement with the RBS results quoted above. The inset shows a comparison between the PR spectra of an as-grown $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ sample and an N^+ -implanted $\text{Al}_{0.35}\text{Ga}_{0.65}\text{N}_y\text{As}_{1-y}$ sample. Although the nominal N concentration is about $x=0.018$, our previous study has shown that only about 12% of implanted N atoms become substitutional.¹⁴ It should be pointed out, however, that the actual N content is not important for the present considerations.

A previous study of the localized nitrogen level in $\text{Ga}_{1-y}\text{Al}_y\text{As}$ has shown that at 2 K the Γ edge shifts above the N level for $y > 0.29$.²¹ Since at this temperature $E_\Gamma = 1.52$ eV and $E_N \geq 1.7$ eV for GaAs ($y=0$), this means that in the impurity limit (low nitrogen concentration), the composition dependence of the E_N level is approximately $dE_N/dy = 0.59$ in $\text{Al}_y\text{Ga}_{1-y}\text{As}$. The dashed line in Fig. 3 represents the change of the E_N position with Al content at room temperature. The figure clearly shows that there is simply no correlation between the location of the X minimum and E_+ and E_- transition energies. The E_+ and E_- transitions are only sensitive to the energy positions of the bottom of the Γ conduction band and the localized N states. An interaction between the X and Γ minima cannot account for the positions of the experimentally observed subband edges. For example, the X band edge lies close to the E_+ transition in the sample with $y=0.35$ and as much as 0.17 eV above this level in GaNAs. This is not possible if an interaction between Γ and X were responsible for the E_+ edge shift. The results shown in Fig. 3 confirm that the localized N level is

responsible for the N-induced modifications of the conduction-band structure. It is worth noting that the change of E_N by about 0.6 eV for y changing from 0 to 1 is very close to the valence-band offset between GaAs and AlAs, $\Delta E_V = 0.55$ eV. This indicates that the energy E_N is practically constant, independent of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy composition, a characteristic feature of highly localized levels that has been previously observed for the N level in $\text{Ga}_x\text{As}_{1-x}\text{P}$ alloys.²²

Although the theoretically predicted interactions between extended band edge states do not play any major role in the N-induced modification of the conduction band of III-N-V alloys, it is possible that they could be of some significance in those instances where the levels lie close to each other. Such may be the case for $\text{Al}_y\text{Ga}_{1-y}\text{N}_x\text{As}_{1-x}$ with $y = 0.35$ when, as shown in Fig. 3, the upper branch edge E_+ is shifted to a slightly higher energy than what is expected for the interaction with the N level only. This shift could be a result of a weak interaction with the energetically nearby X , and/or L minima. Also large hydrostatic pressure measurements in $\text{Ga}_x\text{In}_{1-x}\text{NAs}$ (Ref. 23) have shown that the E_- transition shifts to a slightly lower energy for pressures higher than 100 kbar, corresponding to the pressure where

the X minimum intersects with the E_- edge. The estimated additional energy shift is of the order of 30 meV. The value is approximately one order of magnitude smaller than the energy shift of E_- resulting from the anticrossing interaction between the Γ edge and the localized N states.

In conclusion, we have studied the effect of nitrogen on electronic band structures in $\text{GaN}_x\text{As}_{1-x}$ and $\text{Al}_y\text{Ga}_{1-y}\text{N}_x\text{As}_{1-x}$ alloys by investigating the optical transitions associated with the Γ and L conduction-band edges. We have shown that the modification of the conduction-band structure is well described in terms of an interaction between localized N states and the extended conduction-band states of the host semiconductor matrix. Also our experimental results demonstrate that the theoretically predicted interactions between extended Γ , L , and X minima states do not contribute significantly to the observed effects.

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