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Origin of the nitrogen-induced optical transitions in $\mathbf{GaAs_{1-x}N_x}$

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The temperature and concentration dependence of optical transitions in $GaAs_{1-x}N_x$ (<3.8 eV) are studied by electromodulated reflectance. These studies suggest that the E_+ transition involves the valence-band maximum at Γ and a singlet state originating from the splitting of the quadruply degenerate conduction band at L. Such a transition, forbidden in pure GaAs, becomes allowed in $GaAs_{1-x}N_x$ due to the strong perturbation of nitrogen doping to the band structure. A similar analysis applied to the transition E_* suggests that it is related either to resonant states evolving from the level created by a single isolated nitrogen impurity in GaAs, or to the splitting of the triplet originating from the L conduction band, induced by a further reduction in symmetry associated with nitrogen pairs.

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Ever since the first report of a giant band-gap bowing,[1] $GaAs_{1-x}N_x$ ($x \lesssim 5\%$) has been the subject of intensive experimental and theoretical investigation. Although it is known that the virtual crystal approximation has limitations for the description of semiconductor alloys,[2] the dramatic deviation observed for $GaAs_{1-x}N_x$ is nonetheless unusual. Along with this unexpected band-gap variation, two new electronic transitions, E_+ and E_*, have been observed in optical spectroscopic studies.[3–5] These findings have posed a challenge to theoretical attempts to model the unusual properties observed. But more than being merely a curiosity, a ternary semiconductor alloy exhibiting a decrease in band gap with a decrease in lattice constant opens up many exciting possibilities for technological applications.

Whereas many of the experimental findings concerning $GaAs_{1-x}N_x$ are undisputed, there are several conflicting models that have been proposed to explain the origin of the abnormal behavior of $GaAs_{1-x}N_x$. For example, according to various authors, the E_+ transition results from a two-level repulsion between the resonant N impurity and the conduction-band minimum,[4] a configuration weighted average of interacting conduction-band extrema,[6] singularities in the conduction-band density of states,[7] or a singlet state derived from L_6^c.[8] Critical to the understanding of $GaAs_{1-x}N_x$, and this class of strongly perturbed alloys in general, is the assignment of this transition as it is likely to account for several of its unusual properties.

In this work, we demonstrate that the E_+ transition most likely originates from a splitting of the quadruply degenerate conduction-band extremum near L due to the broken translational invariance. In addition, we suggest that the conduction-band state associated with the E_* transition involves either nitrogen related conduction-band resonant states that evolve from the resonant state produced by an isolated nitrogen impurity in the conduction band of GaAs, or a further splitting of the L conduction-band states due to the reduced point group symmetry associated with nitrogen pairs.

The samples used in this study were grown epitaxially from either molecular-beam epitaxy or organometallic vapor phase epitaxy on (001) GaAs substrates. The samples were nominally undoped and grown on n-type substrates. The typical epilayer thickness is 0.2 μm. From x-ray-diffraction, most samples with concentrations below 1.5% were strained. The details on growth conditions have been published elsewhere.[5,9,10] The nitrogen concentration was determined from x-ray-diffraction. Modulation spectroscopy was used for measuring the energy of optical transitions. Most spectra were modeled using the third-derivative line shapes proposed in Ref. 11. From this modeling, the energy of the critical point, the broadening parameter, and the relative intensity can be reliably extracted. The samples were studied in contactless or direct-contact mode. In contactless mode, a transparent electrode (an indium tin oxide or inconel coated glass plate) is brought in close proximity with the sample.[12] This mode usually gave satisfactory signal levels and was preferred for the measurement of the lowest energy transitions. However, higher sensitivity and signal levels can be achieved using a direct-contact configuration. In this configuration, $\sim$10 Å Ti and $\sim$80 Å Au contact layers were evaporated onto the sample. The value of the internal electric field achieved in this mode can be much higher. This mode was preferred for extracting very weak features such as $E_+ + \Delta_0$ and E_*.

Figure 1 shows a direct-contact electroreflectance spectrum measured on $GaAs_{0.99}N_{0.01}$. The solid line is a fit using the line shape appropriate for each transition. Seven distinct transitions are observed, three of them involving the spin-orbit split valence bands. The energy dependence of these transitions on nitrogen composition is discussed next.

Figure 2 shows the energy of all the transitions measured in this work. All measurements were done at 80 K and the critical-point energy was extracted from the best fit using the models mentioned above. The fundamental band gap of the alloy E_0 involves the zone-center valence (Γ_{8v}) and conduction band (Γ_{6c}). As can be seen, the band gap shifts rapidly to lower energy with increasing N doping. For simplicity, all transitions involving regions of the Brillouin zone located

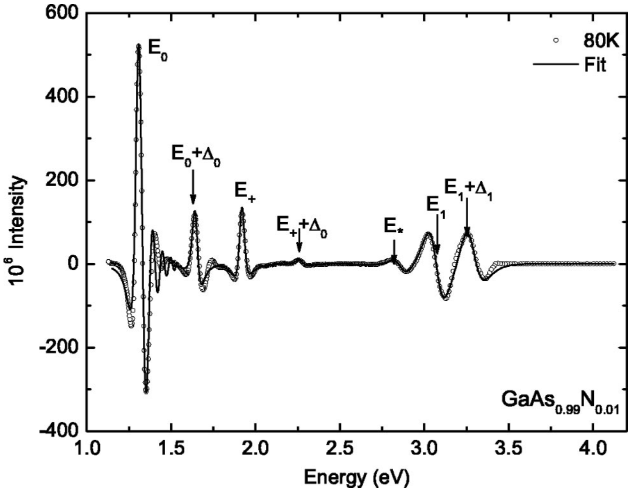

FIG. 1. Electroreflectance spectrum from $GaAs_{1-x}N_x$ with a nitrogen composition of 1.0%. The solid line is a fit to the spectra.

close to the L point will be referred to as L bands (the transition E_1 involves a region of the Brillouin zone close to the L point, between the $\Lambda_{4v,5v}$ valence and Λ_{6c} conduction bands). E_1 shifts to higher energies at a moderate rate of ≈ 24 meV/% N. Transitions involving the spin-orbit split-off valence bands, $E_0+\Delta_0$ and $E_1+\Delta_1$, are also observed. The transitions of main interest are E_+ and E_*. E_+ shifts to higher energies at a rate of 94 meV/% N, which corresponds to about 60% of the observed band-gap reduction. The E_* transition shifts to lower energy at a rate of 52 meV/% N, which is significantly lower than that of E_+. The conduction-band states associated with E_+ and E_* are discussed next.

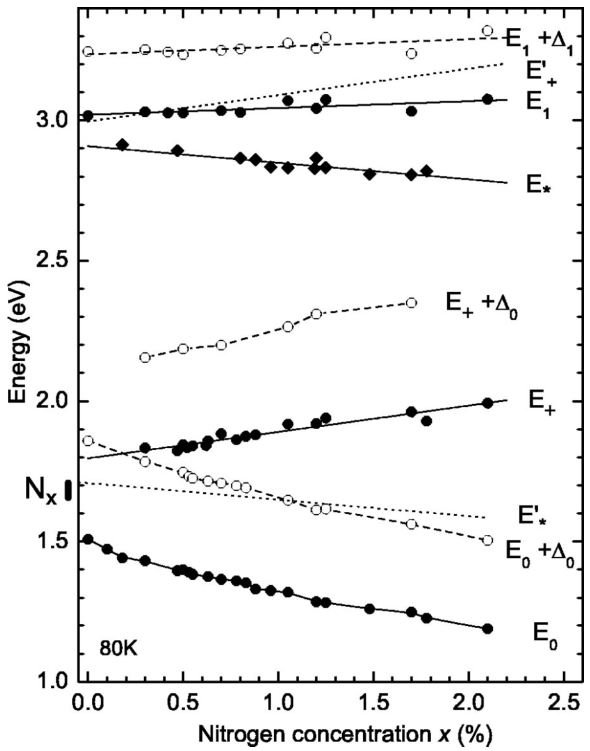

FIG. 2. Concentration dependence of the optical transitions in $GaAs_{1-x}N_x$ measured at 80 K. The transitions denoted E'_+ and $E*'$ duplicate E_+ and E_*, but are translated by $+1.2$ eV and -1.2 eV, respectively.

It was first reported that E_+ arose from the two-level interaction between the nitrogen resonant level (N_x) and the conduction-band minimum of GaAs at Γ.[4] This model known as the band anticrossing model was appealing because the giant band-gap lowering could be explained in terms of a simple two-level repulsion. Due to the number of adjustable parameters, the band anticrossing model is quite versatile in modeling other phenomenological observations,[13] but suffers from some inconsistencies[14] and fails to provide an insightful view on this novel class of alloys. Building from the concept of band repulsion, other more sophisticated models have been proposed that explain the band-gap reduction in terms of a disorder-induced intraband coupling between conduction-band minima.[6,7,15] Unfortunately, these models do not account well for the origin and characteristics of E_+. In contrast to these earlier reports, we assign the conduction-band state of E_+ to the L-derived singlet $a_1(L_6^c)$. This assignment has been recently proposed in the theoretical model of Szwacki *et al.*[8] To support this assignment, we show that the energy of E_+ extrapolates to an energy close to that of the degenerate L_6^c secondary minimum, the temperature dependence of this transition is characteristic of a transition involving the L_6^c-Γ_8^v band edges, and the line shape of the E_+ transition is characteristic of a well-defined band-edge transition and not of that arising from a collection of interacting impurity and host states.

The presence of nitrogen breaks the translational symmetry of the lattice, splits the degeneracy of L_6^c [into a $a_1(L_6^c)$ singlet and a $t_2(L_6^c)$ triplet] and X_6^c [into $a_1(X_6^c)$ and a $e_2(L_6^c)$ doublet],[16] and induces intraband coupling.[17] As a result, forbidden transitions in GaAs become optically allowed.[8] Figure 2 shows the dependence of E_+ on nitrogen concentration. A linear regression applied to the data yields an energy value of 1.796 ± 0.020 eV (Ref. 29) at $x=0$. While the experimental data are best represented by a linear fit, it is not possible to rule out a possible quadratic dependence for E_+. Applying a quadratic fit (not shown) results in slightly smaller extrapolated value of 1.770 eV. The impurity level produced by an isolated nitrogen atom resonant with the conduction band is located between 1.670 and 1.700 eV.[18] This level is therefore at least 70 meV below the extrapolated values obtained for E_+ using a quadratic fit. Figure 2 also shows the energy dependence of E'_+ which is simply that of E_+ translated to a higher energy by 1.2 eV. This energy corresponds to the difference between the Γ_8^v maxima and the $L_{4,5}^v$ minima.[19] As is evident, E'_+ at $x=0$ is located close to E_1 (3.02 eV), indicating that both transitions might originate from the same conduction-band state as has been suggested in the electronic band-structure calculation of Szwacky and Boguslawski.[8] To further support this assignment, we show that the temperature dependence of E_+ agrees very well with the measured temperature dependence of the L_6^c band minima with respect to the Γ_8^v maxima, a necessary requirement for this assignment. Figure 3 shows

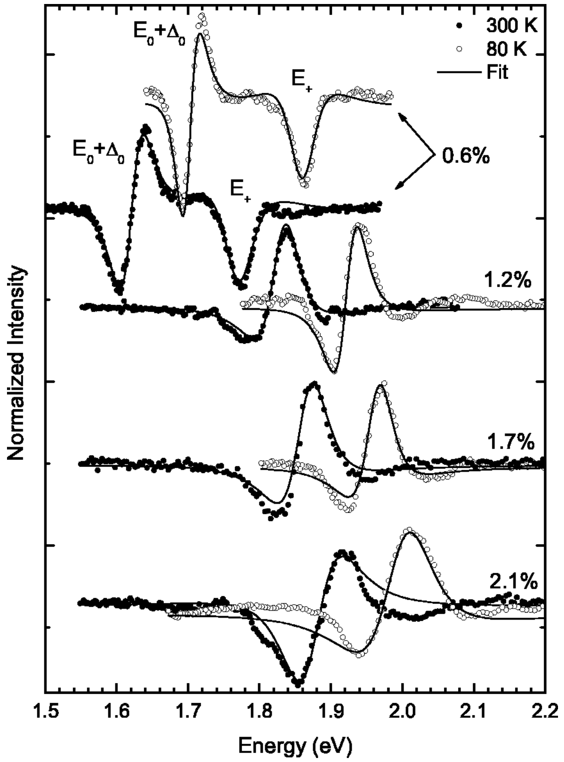

FIG. 3. Spectra of E_+ at 80 (○) and 300 K (●) for several nitrogen compositions. The lines are a fit to the spectra. The low-energy part of the 80-K spectra was truncated for clarity.

the spectra for E_+ measured at 80 and 300 K for several nitrogen compositions. The experimental spectra (circles) are well modeled using the theoretical line shapes (solid line). Panels (b) and (c) of Fig. 4 show the temperature induced shift measured between 80 and 300 K, as a function of nitrogen concentration for E_+ and E_0, respectively. The horizontal dotted lines show the expected energy shift for the fundamental gap[20] and the Γ_8^v-L_6^c band edges[21] of GaAs. The temperature dependence of E_0 appears to be slightly reduced with respect to GaAs as x increases, but it is still within the error bars.[30] The temperature shift of E_+ is consistently larger than the temperature shift found for E_0 for all samples studied, but smaller than the expected temperature shift of E_1.[22] For GaAs, the temperature sensitivity of the L_6^c with respect to the Γ_8^v valence-band edge is 15% and 36% higher than that relative to the Γ and X conduction-band minima, respectively.[21] Assuming that $a_1(L_6^c)$ has characteristics similar to that of L_6^c, the agreement between the temperature dependence of E_+ and that of the GaAs Γ_8^v-L_6^c band edges supports the suggestion made above that the conduction-band state involved is related to the $a_1(L_6^c)$ singlet that originates from the quadruply degenerate conduction-band state near L.

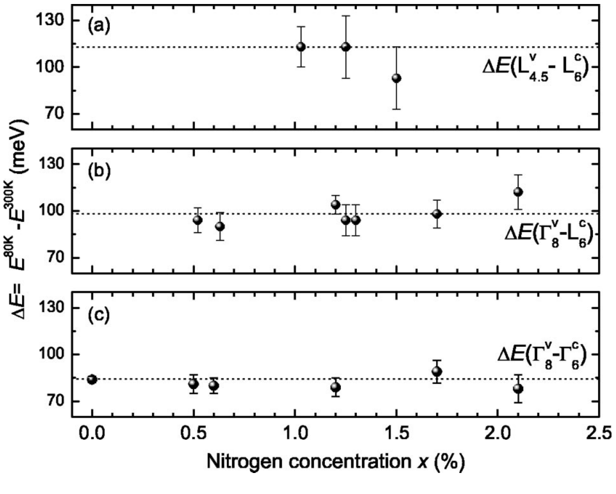

FIG. 4. Temperature shift between 80 and 300 K for (a) E_*, (b) E_+, and (c) E_0. The dotted lines show the expected shift for some GaAs band edges.

We also find that the broadening parameter of E_+, which is proportional to the width of the optical transition, is reminiscent of a well-defined band-edge transition (see Fig. 1). For example, the broadening parameter of E_+ consistently tracks that of $E_0+\Delta_0$, being only 6% larger on average over the entire concentration range studied. We find it unlikely that such a small broadening parameter is characteristic of a resonant level evolving from the interaction of resonant impurity states with a single or multiple host bands, since the energy of the nitrogen levels being very sensitive to the nitrogen configuration and the number of possible configurations quickly increasing in the concentration range studied would result in a broad linewidth. Instead, we associate this small broadening parameter to a well-defined host band-edge transition. With increasing nitrogen concentration, the broadening parameters of E_1 and $E_1+\Delta_1$ increase much faster that that of E_0. This anomalous broadening is simply associated with the presence of an additional transition located between E_1 and $E_1+\Delta_1$ involving $a_1(L_6^c)$ and the valence-band extremum originating from $L_{4,5}^v$ (see E'_+ in Fig. 2). Other experimental findings also support this assignment: Raman experiments have shown that an intensity resonance of the L-point phonons occur at E_+;[23] resonant Raman studies report a similar transition;[24] the pressure dependence of E_+ at low pressure is similar to that of the L conduction band;[4] ellipsometry measurements revealed a weak transition above $E_1+\Delta_1$ at high nitrogen concentration;[25] ballistic electron emission spectroscopy studies revealed that a L-like band shifting to higher energy with nitrogen concentration;[26] the electron effective mass reported is consistent with a $a_1(\Gamma_6^c)$-$a_1(L_6^c)$ mixing;[27] and the reduced bowing coefficient observed for InGaAs$_{1-x}$N$_x$ (Ref. 28) can be related to the larger energy separation between L_6^c and Γ_6^c hence reducing the band interaction.

Another new transition labeled E_* has recently been observed in GaAs$_{1-x}$N$_x$.[5] E_* appears as a broad and very weak transition on the lower energy side of E_1 and has only been observed in direct-contact electroreflectance. Figure 5 shows three representative spectra measured at 80 and 300 K. The solid line shows a fit taking into consideration the M_1 nature of the E_1 and $E_1+\Delta_1$ critical point[31] and it fits the data remarkably well. As can be seen from Fig. 2, E_* moves to lower energy at a rate of ≈ -59 meV/% N and it extrapolates, at $x=0$, to 2.91 ± 0.034 eV. While E_+ is observed

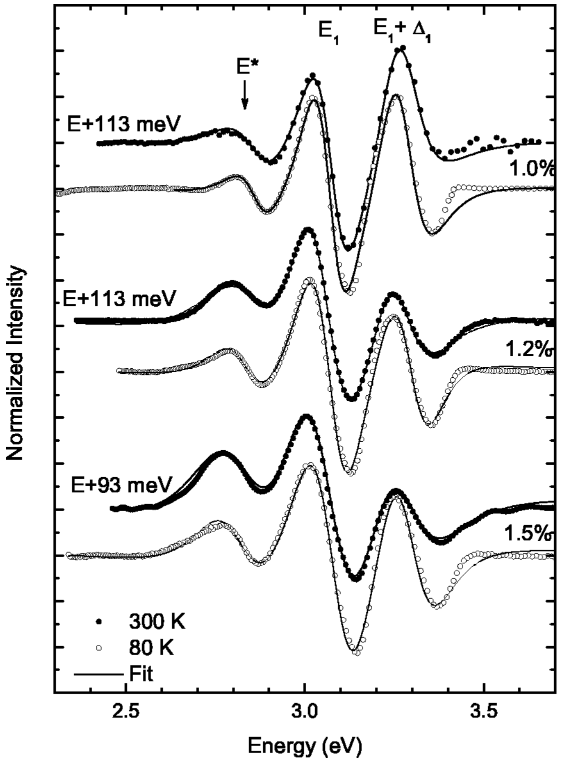

FIG. 5. Spectra of E_*, E_1, $E_1+\Delta_1$ at 80 (○) and 300 K (●, shifted to higher energies by the energy indicated). The lines are fit to the spectra.

because of a relaxation of selection rules due to the lack of translational symmetry, a similar origin for E_* is excluded. For example, assigning it to a transition from Γ_8^v to $a_1(X)$ is dismissed since this would extrapolate to a much lower energy (1.98 eV). The value of $E_*(x\rightarrow 0)$ coincides with the energy of a transition between the L_6^v split-off valence and the Γ_6^c conduction band. However, this transition should be accompanied with a low-energy transition related to the $L_{4,5}^v$ band and additionally its energy dependence on nitrogen concentration should be comparable to that of E_0. Since neither of these conditions are satisfied, we dismiss this possibility.

Following a similar approach taken in Ref. 5, we recast E_* by 1.2 eV to lower energy. The result is shown by the line labeled E_*' on the graph. We find that E_*' extrapolates at $x\rightarrow 0$ to 1.710 ± 0.034 eV and is close to the energy of N_x which corresponds to the resonant level produced by an isolated nitrogen atom in GaAs. Photoluminescence experiments have shown that the isolated nitrogen impurity state becomes a bound state at hydrostatic pressures exceeding ~22 kbar. At ambient pressure at low temperature, the expected position of this nitrogen level extrapolates to about 150–180 meV above the conduction-band mimimum.[18] This energy range is shown in Fig. 2 by the vertical bold line close to the energy axis. This coincidence suggests that E_* might be related to the nitrogen-induced resonant band in $GaAs_{1-x}N_x$.

Panel (a) of Fig. 4 shows the energy shift of E_* between 80 and 300 K. While the uncertainty is relatively large, the temperature induced shift is the largest compared to that of E_0 and E_+ and is very close to the temperature dependence of E_1 for GaAs,[22] indicating that E_* emulates the temperature dependence of the L valence- and conduction-band edges. This rather high-temperature sensitivity is surprising if we assume that E_* originates from the N_x localized resonant level. It has been shown that the wave function of the nitrogen related resonant state projects to all regions of the Brillouin zone of GaAs, demonstrating that this state is highly delocalized in momentum space. Therefore, the temperature sensitivity of this resonant state should approximate the temperature sensitivity of the conduction-band states averaged over a large region of the Brillouin zone. This average should be much smaller than that observed in Fig. 4(a). Therefore this result appears to contradict the tentative assignment made above.

It is possible that E_*, just like E_+, originates from the highly perturbed L conduction band. Taking into consideration interactions between nitrogen atoms, the overall symmetry is further reduced and is only a subset of the point group T_d. Therefore, the formation of nitrogen pairs necessarily implies that the degeneracy of $t_2(L_6^c)$ must be broken down into either three singlets or one doublet and one singlet. It is possible that both E_+ and E_* share the GaAs conduction-band L point as origin. This alternative explanation is supported by results obtained from resonant Raman measurements, where the three resonant features located at energies higher than the band gap extrapolate to L_6^c at $x\rightarrow 0$.

In conclusion, we find that the E_+ transition most likely involves the L-derived singlet $a_1(L_6^c)$. This transition, optically forbidden in pure GaAs, results from the strong perturbation caused by nitrogen on the host band structure. Evidently, any explanation of the large band gap bowing observed in $GaAs_{1-x}N_x$ must take into account the multiple intraband coupling induced by nitrogen's strongly localized impurity potential and its surrounding lattice relaxation. The dominant contribution to the band-gap reduction appears to be from the interaction between $a_1(\Gamma_6^c)$ and $a_1(L_6^c)$. Finally, two competing mechanisms have been proposed for the origin of E_*. This transition originates either from a nitrogen resonant state evolving from N_x or from the lifted degeneracy of $t_2(L_6^c)$ induced by the reduction in symmetry associated with the presence of nitrogen pairs.

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[29] The uncertainty is taken as the difference between the minimum and maximum extrapolated values allowed by a 95% confidence band.

[30] The error on the critical-point energy is taken as 10% of the broadening parameter.

[31] E_* was modeled using an M_1 critical point. While it might not be the most appropriate line shape, the error that this assumption would add to the critical-point energy would be small (Ref. 22).