Analysis of band anticrossing in GaN$_x$P$_{1-x}$ alloys

I. A. Buyanova, M. Izadifard, A. Kasic, H. Arwin, and W. M. Chen

Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden

H. P. Xin, Y. G. Hong, and C. W. Tu

Department of Electrical and Computer Engineering, University of California, La Jolla, California 92093-0407, USA

Temperature-dependent absorption, photoluminescence excitation, and spectroscopic ellipsometry measurements are employed to accurately determine compositional and temperature dependences of the conduction band (CB) states in GaNP alloys. The CB edge and the higher lying Γ_c CB minimum (CBM) are shown to exhibit an apparently anticrossing behavior, i.e., the N-induced redshift of the bandgap energy is accompanied by a matching blueshift of the Γ_c CBM. The obtained data can be phenomenologically described by the band anticrossing model. By considering strong temperature dependence of the energy of the interacting N level, which has largely been overlooked in earlier studies of GaNP, the interacting N level can be attributed to the isolated substitutional N$_P$ and the coupling parameter is accurately determined.

Insertion of nitrogen in conventional III-V alloys, such as GaAs and GaP, strongly affects their electronic structure, leading to a wealth of fascinating physical properties inherent to the forming dilute nitrides alloys. They include: the giant bowing of the bandgap energy accompanied by the splitting of the conduction band (CB) states, the enhanced nonparabolicity of the CB dispersion, the unusually weak dependence of the bandgap energy on applied pressure and measurement temperature, etc.[1,2] These properties have been found to be very desirable for various applications in optoelectronic and photonic devices, further attracting interest in novel dilute nitrides. The N-induced modifications in the band structure have been attributed to a large mismatch between sizes and electronegativity between the N atom and other group-V element of the host lattice, which causes breaking of translational symmetry and thus promotes strong mixing of the CB states.[3] Alternatively, the bandgap bowing can be described by the interaction between N-related localized states and the Γ_c CB minimum (CBM) of the same symmetry, by the so-called band anticrossing (BAC) model.[4–7] This rather simple model provides a surprisingly satisfactory phenomenological description of the N-induced effects on the band structure of dilute nitrides and is thus found attractive in conveniently predicting the change of the bandgap energy, also useful for, e.g., device modeling.

According to the BAC model, the interaction between an a_1 localized N state and extended CB states of the same symmetry (i.e., the Γ_c minimum) splits the CB into two subbands, with their energies described by the equation[4–7]

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

Here $E_\Gamma(k)$ is the dispersion relation of the Γ_c CB edge, E_N is the energy of the localized N state, and x is the N fraction. All energies are measured with respect to the valence band (VB) maximum. C_{NM} is the coupling parameter determined by the strength of coupling between the localized and ex-

tended states and depends on the semiconductor matrix. The bandgap energy is given by the energy of the lower subband edge $E_-(0)$. Equation (1) allows to predict compositional, temperature, and pressure dependences of the involved CB states in the alloys, as well as to estimate the corresponding electron effective masses,[7] provided that the values of E_N and C_{NM} are accurately known.

For Ga(In)NAs alloys the energies of the E_+ and E_- states can be measured with rather high precision from reflectance studies. This has ensured an accurate determination of both E_N and C_{NM} values in these materials, e.g., $E_N = 1.64$ eV and $C_{NM} = 2.7$ eV for GaNAs.[6] As the obtained energy position of the interacting N state has been found very close to the level of the isolated substitutional N impurity (N$_{As}$), which is known from previous studies of GaAs:N, the interacting localized N state was attributed to the level of N$_{As}$. On the other hand, for GaNP alloys the situation is less straightforward. First of all, the bandgap energies in GaNP were often deduced from photoluminescence (PL) measurements. This can cause substantial errors in the determined BAC parameters, as the PL transitions in GaNP alloys even at room temperature arise from deep N-related states, not due to band-to-band recombination.[8] (Even though the PL measurements were sometimes complemented by the photoreflectance studies,[5] the weak intensity of the reflectance signal and its overlap with the strong background PL should inevitably lead to a large errorbar in the determined values.) Secondly, contrary to Ga(In)NAs, the interacting localized N state was attributed[5,6] to some kind of average over various N-related states, rather than to a certain N-related level. This is because the obtained E_N value ≈ 2.15–2.18 eV did not match any known N-related level in GaP. This has therefore raised doubts on the physical meaning of the corresponding level and thus overall validity of the BAC approach.

In this work we employed temperature-dependent optical absorption, photoluminescence excitation (PLE), and spectroscopic ellipsometry measurements aiming to obtain accurate compositional and temperature dependences of the CB
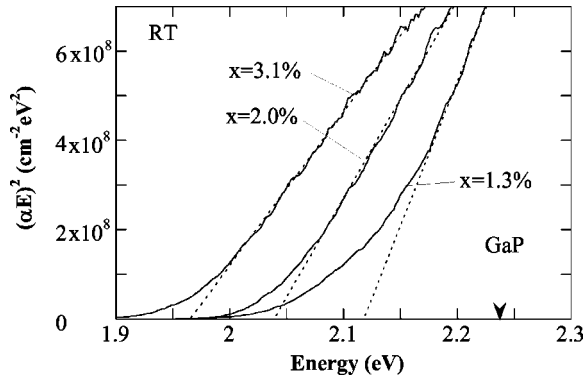
FIG. 1. Spectral dependence of the absorption coefficient measured at room temperature (RT) from the GaNP alloys with the specified N compositions. The bandgap energies were obtained by extrapolating the linear part of $(\alpha E)^2$ to zero, as shown by the dashed lines.

states in GaNP. We show that the energy positions of the CB edge and the higher lying CB states that evolve from the Γ_c CBM exhibit an apparently anticrossing behavior. The BAC model is shown to provide a good description of the obtained data. By taking into account the previously overlooked temperature dependence of the localized N levels, the energy of the interacting N level is shown to coincide with that of the isolated, substitutional N_P. This analysis also provides accurate determination of the coupling parameter for GaNP alloys.

The GaNP epilayers (with a thickness of $0.25-0.75~\mu$m) studied in this work were grown by gas-source molecular beam epitaxy on (100) GaP substrates. The alloy composition x was determined by theoretical dynamical simulations of measured x-ray rocking curves. The band gap energy of the alloys (to be referred to as the E_- state in the following discussion) was determined from optical absorption measurements. The measurements were carried out in a variable temperature cryostat using a halogen lamp as a light source and a double grating spectrometer with a silicon avalanche detector for spectral dispersion and detection. The energy positions of the higher lying CB state which evolves from the Γ_c CBM (to be referred to as the E_+ state below) were determined from spectroscopic ellipsometry and PLE studies. Spectroscopic ellipsometry measurements were carried out at room temperature (RT) using a rotating-analyzer ellipsometer equipped with a 75-W Xe lamp as a light source. Data were taken at multiple angles of incidence with a spectral resolution of 4 meV. PLE measurements were performed at 2 K using a dye laser as an excitation source. The resulting PL was detected by a GaAs photomultiplier after passing through a double grating monochromator.

Figure 1 shows representative results from the performed absorption measurements. For photon energies E exceeding the GaNP bandgap, spectral dependence of the absorption coefficient α obeys a linear function in coordinates $(\alpha E)^2$ vs E, characteristic for direct band gap semiconductors, as was discussed in detail in Ref. 9. An extrapolation of the linear part of the dependence to zero value of $(\alpha E)^2$ provides band-
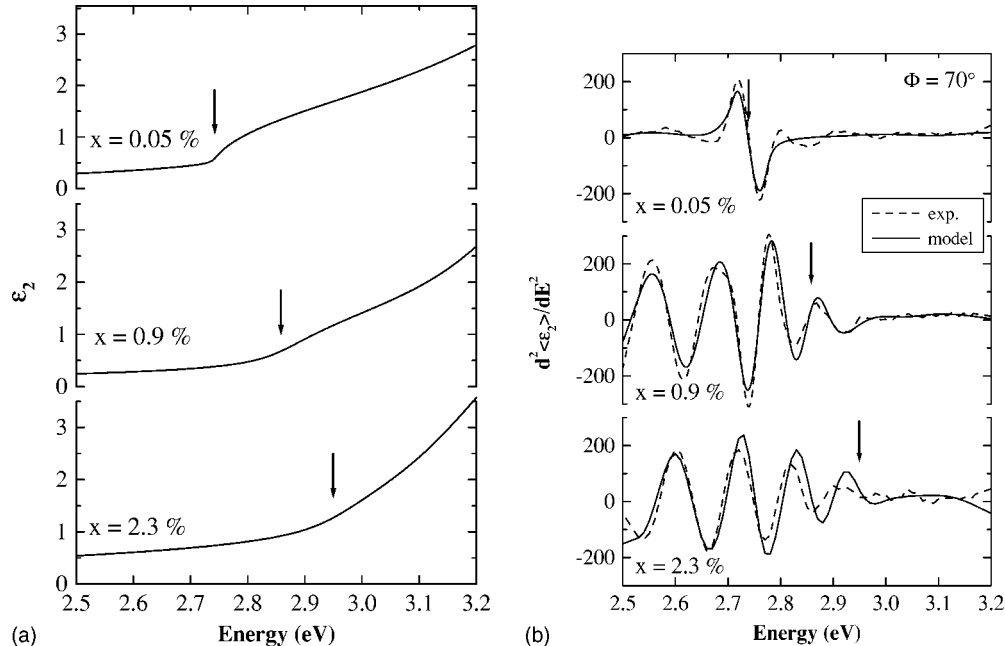

FIG. 2. (a) The imaginary part of the dielectric function obtained from the GaPN layers with the specified N contents measured by spectroscopic ellipsometry. The onset of the absorption is clearly blueshifted with increasing N content. (b) Second derivative spectra of the imaginary part of the pseudodielectric function $\langle\varepsilon_2\rangle$ at an angle of incidence of 70°. Dashed lines are experimental data, and solid lines are calculated model dielectric function spectra. Vertical markers indicate the positions of the E_0 critical point energy values obtained from the data regression analysis, which was directly performed on the basis of the $\langle\varepsilon_2\rangle$ data in the range between 2.5 and 3.2 eV. Below the Γ point transition, Fabry-Perot interference oscillations are present, which become damped with decreasing photon energy due to a considerable absorption tail. The interference effects were described in a self-consistent way using a two layer model that accounts for the substrate, the GaNP layer, the native oxide and the ambient.
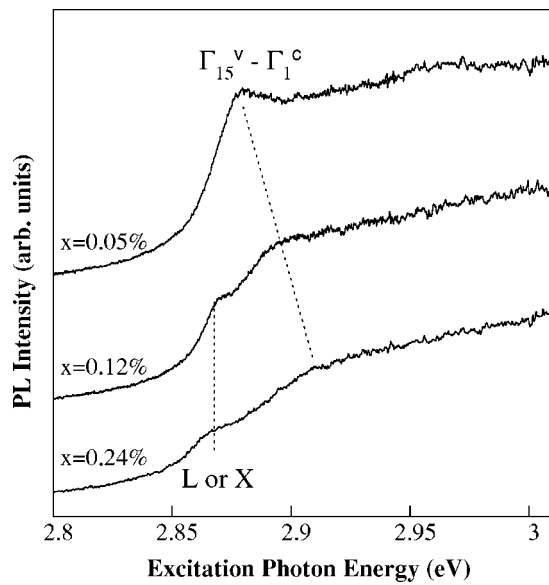
FIG. 3. Effect of N incorporation on the PLE spectra measured in the vicinity of the Γ_{15}^v-Γ_1^c transition for the specified N compositions. The additional feature is probably due to transitions from Γ_{15}^v to the L or X CB state, which is beyond the scope of the present paper. The spectra are shifted vertically for clarity.

gap energies of the alloys (or E_- values). Examples of the performed spectroscopic ellipsometry studies are depicted in Fig. 2. In this case, the spectral positions of the $\Gamma_{15}^v - \Gamma_1^c$ transition (the E_+ state), indicated by vertical markers in Fig. 2, were determined by the parametric line shape regression analysis of the measured pseudodielectric function $\langle \varepsilon \rangle$. In the analysis, a composite model dielectric function based on the one-electron interband-transition approach, as described, e.g., in Refs. 10–12, was employed with the $\Gamma_{15}^v - \Gamma_1^c$ transition being described by a critical point of the 3D M_0 type and assuming parabolic bands. The same information was also obtained by measuring low temperature PLE spectra of N-related emissions, based on the spectral position of the $\Gamma_{15}^v - \Gamma_1^c$ excitonic transition—see Fig. 3. The E_+ position was corrected by 5 meV to account for the binding energy of a direct exciton in GaP.[13] As the PLE features become broad for the GaN$_x$P$_{1-x}$ alloys with $x > 0.6\%$, this method was only employed for the alloys with low N contents. The obtained results are summarized in Fig. 4 where compositional dependences of the E_- and E_+ states measured at 2 K and RT are shown together with a summary of the previously published data for GaNP alloys. The deduced values of the E_- and E_+ states at RT [Fig. 4(b)] are in very good agreement with the previous results from absorption[14] and ellipsometry[11] measurements. On the other hand, the bandgap energies have obviously been underestimated in Ref. 5, as they were deduced from the maximum position of the RT PL emission of the impurity origin.

As obvious from Fig. 4, N incorporation causes a strong redshift of the GaNP bandgap accompanied by a comparable blue shift of the higher lying Γ_c CB state. (The detailed physical mechanism responsible for these N-induced modifications of the CB states is beyond the scope of this paper and is discussed in detail in Ref. 15.) The apparently anticrossing
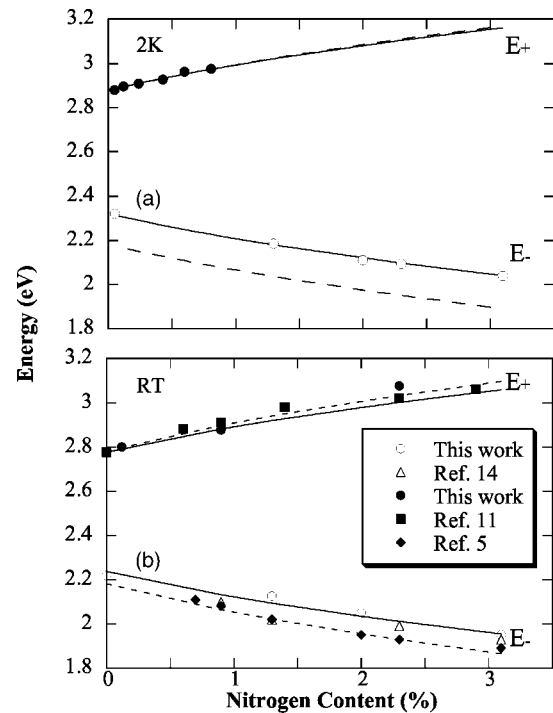

FIG. 4. Compositional dependence of the CB edge (E_-) and the Γ_c CB minimum (E_+) in the GaNP alloys at 2 K (a) and RT (b), respectively. Solid lines represent fitting curves using Eq. (1) and parameters deduced in this work and provide very good agreement with the experimental data (dots). The E_+ and E_- positions expected from Ref. 5 are shown by the dashed curves.

behavior of the E_- and E_+ CB states at both temperatures can be described by Eq. (1) with the same coupling parameter $C_{NM} = 2.76$ eV. In is interesting to note that the obtained value is very close to that deduced for GaNAs alloys, i.e., $C_{NM} = 2.70$ eV, which points towards a similar origin for the coupling, e.g., a similar degree of hybridization of extended and localized states in both materials. As to the energy position of the E_N state, our new results yield $E_N = 2.33$ eV at 2 K and $E_N = 2.25$ eV at RT, i.e., it is temperature dependent. At a first glance, this result is rather surprising taking into account a localized character of the N-related states. We will show below, however, that the obtained E_N value in fact coincides with the energy level of the isolated substitutional N atom N_P, clarifying the origin of the interacting localized N state as being due to the N_P.

Indeed, the energy position of the N-bound exciton in GaP (A line) is 2.317 eV at 2 K with an exciton binding energy of $E_b^{ex} = 11$ meV.[16] As the binding energy of an electron at the N atom is known[17] to form the major portion of E_b^{ex}, this yields the energy position of the N-related level at around 2.33 eV, in excellent agreement with the deduced E_N value at 2 K. With increasing temperature, the spectral position of the A line was shown to shift towards lower energies following the bandgap of GaP.[18,19] The exciton binding energy remains temperature independent,[20] however, implying a strong temperature dependence of the N_P level position, as shown by the dotted line in Fig. 5. The energy position of the N_P level RT is 2.25 eV,[19] in excellent agreement with the $E_N = 2.25$ eV deduced from the BAC fitting in the present study.
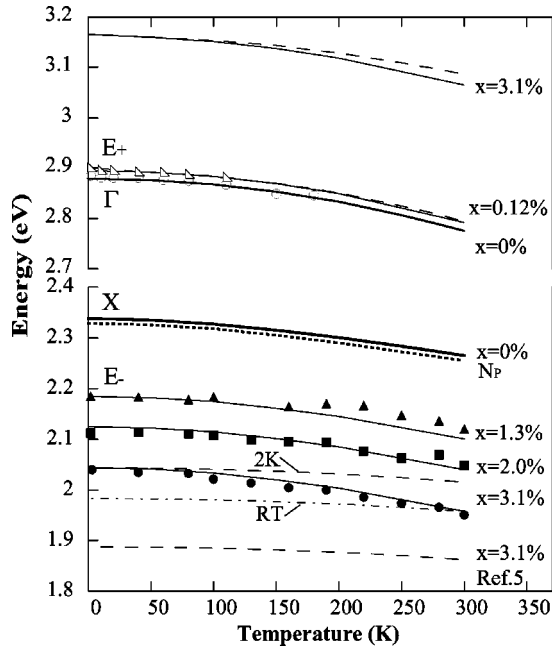
FIG. 5. Temperature dependence of the CB edge (E_-) and Γ CB minimum (E_+) measured for the GaNP alloys with the specified N compositions. Also shown are the $\Gamma(T)$ and $X(T)$ (thick solid lines) (Ref. 21) and the previously determined $N_P(T)$ (dotted line) dependences (Refs. 18–20) employed in the fitting using Eq. (1). The results of the fitting are shown by the thin solid lines. The dashed and dashed-dot lines are fitting curves obtained for the $GaN_{0.031}P_{0.969}$ alloy by neglecting temperature dependence of the E_N position and using the corresponding values deduced at 2 K and RT, respectively. The lowest dashed line shows temperature dependence of the E_- position for the $GaN_{0.031}P_{0.969}$ alloy, estimated by using the BAC parameters from Ref. 5.

Consistently, the BAC model also provides a very good description of the overall temperature dependence of the E_+ and E_- states in GaNP alloys. This is shown in Fig. 5, where the data points of the experimentally determined E_+ and E_- positions are plotted as a function of measurement temperature for several N compositions, together with the $\Gamma_c(T)$ (Ref. 21) and $N_P(T)$ (Refs. 18 and 19) dependences employed in the fitting. The results of the fitting are shown by the thin solid lines and are in very good agreement with the experimental data. On the contrary, the assumption of a temperature independent E_N level that was employed in earlier studies leads to much slower thermal variations of the E_- state, inconsistent with the experimental observations (shown by the dashed and dash-dotted lines for the $GaN_{0.031}P_{0.969}$ alloy with E_N level fixed at 2.33 and 2.25 eV, respectively).

We should point out that the observed strong temperature variation of the N level is rather surprising for a deep-level defect in a semiconductor, which adds to controversies of the N behavior in III-V compounds (see, e.g., Ref. 22, and references therein). Even though the N_P level in GaP exhibits typical deep level behavior with electron binding via short range potential, its temperature dependence is very similar to that characteristic for shallow impurities, i.e., the energy position of the A line in GaP follows the bandgap variation with temperature.[18,19] Similar behavior is also observed even for

deeper N states (e.g., related to N-N_i pairs and N clusters), judging from the energy shifts of the corresponding excitonic transitions with temperature, in spite of their insensitivity to pressure and alloying. In principle, a basic treatment of the isoelectronic impurity models N potential by a short range Koster-Slater potential that attracts the CB electron.[23,24] In addition to electronegativity difference between N and P atoms, the lattice distortions in the vicinity of N were shown to play a decisive role in determining the strength and the range of this potential, and thus the energy level of the related bound state.[3,22,24] To a certain degree, this local distortion can be affected by temperature-induced changes in deformation potential, leading to the shift of the N levels. Alternatively, Aspnes *et al.*[25] have shown that the energy of the N level in GaP(As) can be approximated from the Koster-Slater Schrödinger equation considering only off-diagonal coupling within the Brillouin zone. Taking into account a low density of states for the Γ CBM, which is by orders of magnitude smaller than that associated with the X and L minima, the E_N energy was deduced as

$$E_N = \frac{1}{2}(E_X + E_L) - \frac{1}{2}[(E_X - E_L)^2 + 4V^2]^{1/2}, \qquad (2)$$

where E_X and E_L are the energy positions of the X- and L-CB minima, V is the Koster-Slater interaction strength. Such approximate description suggests temperature dependence of the N level to a degree similar to that for the X and L CBM, consistent with experimental observations. [A lack of experimental data on $E_L(T)$ dependence has prevented us from quantitative determination of the $E_N(T)$ dependence predicted by Eq. (2).] Naturally, a strong variation of the E_N position is then also expected for GaAs due to similar origin of the N-related states in both compounds, which is more challenging to verify experimentally as the N levels are resonant with the CB states. This has largely been overlooked in the earlier BAC analysis of the temperature behavior of the bandgap energies (or E_-) in Ga(In)NАs alloys,[26] where the E_N level was believed to be temperature independent based on the localized nature of the N-related state and its known stability under applied hydrostatic pressure. On the other hand, the assumption of the temperature variation of the E_N position in GaInNАs alloys was crucial to account for the experimentally observed temperature-induced shift of the E_+ transition.[27] This seeming contradiction can be explained within the BAC model by the difference between the origin of the E_- and E_+ states.[27] Indeed, according to the BAC model, the E_+ state in GaInNАs is developed mainly from the localized N level and thus should largely follow its properties. On the other hand, the E_- state is mainly built up from the extended CB states and is therefore less sensitive to the thermal variation of the E_N position. The level ordering is reversed in GaNP alloys, i.e., the N level is now the lowest in energy and is thus suggested to evolve into the CB edge, whereas the E_+ state stems from the Γ CBM. This implies strong sensitivity of the CB edge to the thermal variation of the E_N position whereas the E_+ transitions should be affected to a much lesser degree—see Fig. 5. Such tendency is indeed consistent with our experiments.

In conclusion, by employing temperature-dependent absorption, spectroscopic ellipsometry, and PLE spectroscopies, we have determined accurate compositional and temperature dependence of the bandgap energy and the Γ_c-related CB states in GaNP alloys. Both states are found to exhibit an apparently anticrossing behavior, i.e., the N-induced redshift of the bandgap energy is accompanied by a matching blueshift of the Γ_c CBM. The obtained data are shown to be well described by the phenomenological BAC model, where the interacting N level can now be related to the isolated substitutional N_P by taking into account previously overlooked temperature dependence of its energy position. The accurate value of the coupling parameter for GaNP alloys is also provided from this study and is shown to be temperature independent. We would like to point out, however, that even though the BAC model provides a very good phenomenological description of the data, it does not seem to be able to account for the detailed physical mechanism responsible for the N-induced modifications of the CB states in GaNP alloys. The conduction band edge of the alloys (E_- state) does not evolve from the E_N level, as suggested by the BAC model, as the energy positions of the N-related levels (monitored via absorption,[10] PL,[8] and PLE[15] measurements) do not change during alloy formation.

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