PHYSICAL REVIEW B, VOLUME 65, 241303(R)

Band anticrossing in $GaP_{1-x}N_x$ alloys

J. Wu,[1,2,*] W. Walukiewicz,[1,†] K. M. Yu,[1] J. W. Ager III,[1] E. E. Haller,[1,3] Y. G. Hong,[4] H. P. Xin,[4] and C. W. Tu[4]
[1]*Materials Sciences Division, Lawrence Berkeley National Lab, Berkeley, California 94720*
[2]*Applied Science and Technology Graduate Group, University of California, Berkeley, California 94720*
[3]*Department of Materials Science and Engineering, University of California, Berkeley, California 94720*
[4]*Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California 92093*
(Received 26 November 2001; published 29 May 2002)

The optical properties of $GaP_{1-x}N_x$ alloys ($0.7\% \leqslant x \leqslant 2.3\%$) grown by gas-source molecular-beam epitaxy have been studied using photoluminescence spectroscopy under hydrostatic pressures up to 133 kbar at 30 K. The peak energy of the band-edge photoluminescence spectrum shows an unusual, nonmonotonic dependence on the hydrostatic pressure. The anomalous results are explained in terms of an anticrossing interaction of localized nitrogen states with the Γ band edge at low pressures and with the *X* band edge at large hydrostatic pressures.

DOI: 10.1103/PhysRevB.65.241303 PACS number(s): 71.20.Nr, 62.50.+p, 78.20.−e

The incorporation of small amounts of nitrogen into III-V semiconductors has dramatic effects on the electronic properties of the resulting III-V_{1-x}-N_x alloys. The isoelectronic substitution of only 1% N for As in GaAs reduces the band gap by more than 0.18 eV.[1–5] The alloying of GaP with less than 1% GaN changes the nature of the fundamental band gap from indirect to direct.[6] These distinctive properties have recently attracted much research attention because of the practical applications of these semiconductor alloys for optoelectronic devices such as light-emitting diodes[7] and multijunction high-efficiency solar cells.[8]

These semiconductor alloys are also of great interest from the fundamental research point of view. Various mechanisms have been proposed to explain the unique *N*-induced changes in the properties of these III-V-N alloys[9–10] We have shown previously that the electronic structure of group III-N-V alloys can be quantitatively described by a band anticrossing (BAC) interaction between the zone-center conduction-band Bloch states ($|\Gamma\rangle$) of the host material and a highly localized nitrogen-derived state ($|N\rangle$).[4,6,10] The BAC interaction results in a conduction-band restructuring of the host semiconductor, an effect previously known for strong extended-localized interacting systems.[11] The localized state is located at about 0.23 eV above the Γ conduction-band edge in GaAs and slightly below the *X* conduction-band edge in GaP. The energy level of the localized N state in GaAs and GaP has been directly observed by photoluminescence spectroscopy.[12] The interaction strength, represented by a parameter $C_{N\Gamma}$, has been determined to be 2.7 and 3.05 eV for $GaAs_{1-x}N_x$[4] and $GaP_{1-x}N_x$,[6] respectively.

On the other hand, since the wave function of $|N\rangle$ is highly localized in real space, its Fourier transform has significant contributions of off-zone-center components in the Brillouin zone. It is, therefore, expected to couple not only with the Γ conduction state, but also with other conduction states such as the *L* and *X* band minima. To date, no systematic experimental study has been reported regarding these off-zone-center couplings between the band states of the host material and the N state in the III-$V_{1-x}N_x$ alloys. In this paper we report our low-temperature investigations on the hydrostatic pressure dependence of the fundamental band gap of $GaP_{1-x}N_x$ alloys, with x varying from 0.7% to 2.3%. Our results show that at high pressures the fundamental band gap shifts to lower energy as a function of pressure, approaching the negative pressure dependence of the *X* band minimum of GaP. The pressure dependence of the fundamental band gap is explained by the interactions of the N localized state with the lowest conduction band of the host GaP.

The $GaP_{1-x}N_x$ samples are epitaxial layers grown on GaP substrates by gas-source molecular-beam epitaxy using a rf plasma nitrogen radical beam source. The layer thickness varies from 0.75 to 0.9 μm. Prior to the growth of the $GaP_{1-x}N_x$ layer, a 0.2-μm GaP buffer layer was deposited on the substrate. The nitrogen concentration of the samples was determined from high-resolution x-ray rocking-curve measurements and theoretical dynamical simulations. A detailed discussion of the sample preparation and x-ray measurements has been reported elsewhere.[13]

The samples were mechanically polished into small chips of $\sim 100 \times 100\ \mu m^2$ in size and a thickness of $\sim 10\ \mu m$, and mounted into gasketed diamond anvil cells for the application of hydrostatic pressure. The pressure medium was a mixture of ethanol and methanol (1:4), and the applied pressure was calibrated by the standard method of monitoring the redshift of the ruby *R*1 line. Photoluminescence (PL) signals were generated in the backscattering geomtery by excitation with the 476.5-nm line of an argon laser and were dispersed by a 1-m double-grating monochromator.

The $GaP_{1-x}N_x$ samples have intense PL visible to the naked human eye even at room temperature. But as we have demonstrated before,[6] the room-temperature PL decreases in intensity as pressure increases, and becomes undetectable at high pressures (e.g., above 35 kbar for $x = 1.3\%$). Cooling down the sample greatly improves the luminescence efficiency. Shown in Fig. 1(a) is the 30-K PL spectrum of a $GaP_{0.977}N_{0.023}$ sample under different pressures. The PL signal decreases in intensity with increasing pressures, but remains detectable to pressures above 100 kbar.

Figure 1(b) shows the peak energy and the integrated area of the PL as a function of pressure. The PL intensity starts to decrease abruptly at $\sim 80 \pm 10$ kbar, the pressure at which

 ©2002 The American Physical Society

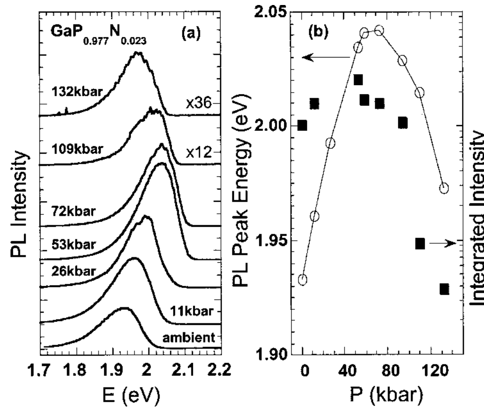

FIG. 1. (a) Photoluminescence spectra of a $GaP_{0.977}N_{0.023}$ sample under different pressures. All the PL spectra were taken at $T=30$ K. (b) Pressure dependencies of the peak energy and the integrated PL intensity of $GaP_{0.977}N_{0.023}$ at 30 K. Note the logarithmic scale of the integrated intensity.

the peak energy reaches its maximum. This phenomenon implies a fundamental change in the nature of the lowest conduction-band edge at this pressure.

As discussed in Ref. 6, at low pressures, the PL signal from $GaP_{1-x}N_x$ corresponds to the direct transition from the lowest conduction band to the top of the valence band. The peak energy of the PL signal blueshifts at a small rate with increasing pressure as a result of the anticrossing between the Γ conduction-band minimum of GaP and the N localized level.[6] The PL peak energy for $GaP_{0.977}N_{0.023}$ as a function of pressure is shown in Fig. 2, together with the results from two other samples with $x=0.007$ and 0.017. The FWHM of the PL peak is about 0.12 eV. It should be noted that N-free GaP did not show a detectable PL signal under the same

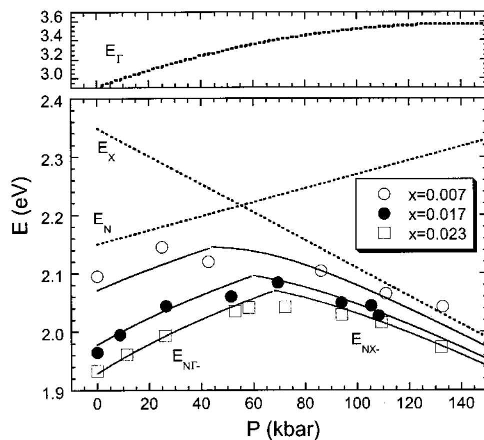

FIG. 2. PL peak energy at 30 K as a function of pressure for three samples with different N concentrations. The dashed lines indicate the pressure dependencies of the N localized state, the Γ band, and the X band minima of GaP. The solid curves are the calculated lowest conduction-band energies for the three N concentrations based on the band anticrossing model. The kinks in the calculated curves indicate the crossover of the nature of the lowest conduction band from N-Γ mixing to N-X mixing. Note the different scale for the upper portion of the plot.

experimental conditions. All three N-containing samples show a similar nonmonotonic pressure behavior. Interestingly, the PL peak energies of all the three samples tend to have the same asymptotic pressure dependence at high pressures. The difference between the peak energies for $x=0.007$ and 0.023 is reduced from 160 meV at ambient pressure to 50 meV at $\sim$110 kbar. As is well known, in GaP the X band minimum (E_X) is located at $\sim$2.35 eV above the valence-band edge at ambient pressure at 30 K,[14] and has a negative pressure coefficient of about -0.0024 eV/kbar.[15] The energy of this minimum is plotted in Fig. 2. It is evident that at high pressures the PL peak energies of all the three alloys approach the indirect band gap (X_c-Γ_v) of the host GaP.

To explain the pressure behavior of the PL of $GaP_{1-x}N_x$ alloys, we describe the conduction-band states by the following dispersion relations derived from the band anticrossing model:[6,10]

$$E_{\pm}(k)=\tfrac{1}{2}\{[E_M(k)+E_{\rm N}]\pm\sqrt{[E_M(k)-E_{\rm N}]^2+4C_{{\rm N}M}^2(k)x}\},\qquad(1)$$

where $E_M(k)$ is the energy dispersion of the lowest conduction band of the host GaP, and $E_{\rm N}$ is the energy of the N localized state, all referenced to the top of the valence band of GaP. The coupling between $|N\rangle$ and the band states of GaP is described by the adjustable parameter $C_{{\rm N}M}$ and is assumed to be k dependent.

The location of E_Γ in GaP as a function of the hydrostatic pressure is well known and can be written as $E_\Gamma(p)=2.9+0.0097\,p-(3.5\times10^{-5})p^2$,[15,16] where $E_\Gamma(p)$ is measured in eV and p is the hydrostatic pressure in kilobars. With the known pressure dependencies of $E_X(p)$ and $E_\Gamma(p)$, we fit the experimental points in Fig. 2 to the lowest edge of the $E_-(k)$ subband calculated from Eq. (1). As is seen in Fig. 2, the pressure dependence of the PL peak energy can be divided into two regimes. At low pressures, the PL is attributed to the direct transitions from the lowest conduction-band edge $E_{{\rm N}\Gamma-}$, which evolves from the $E_{\rm N}$ level through a band anticrossing interaction with E_Γ, to the top of the valence band. The pressure coefficient for this transition is positive and similar to that of the $E_{\rm N}$ level. At higher pressures the E_X edge shifts downwards, and the $E_{{\rm N}X-}$ edge resulting from the anticrossing interaction between E_X and $E_{\rm N}$ becomes the lowest conduction-band edge. The indirect transitions from $E_{{\rm N}X-}$ to the top of the valence band are responsible for the PL signal in this pressure regime. The abrupt decrease of the PL intensity shown in Fig. 1(b) is consistent with the predicted change in the character of the fundamental band gap.

Although considerably weaker, the indirect transitions are still possible, because the localized N centers partially break the translational invariance of the crystal and relax the wave-vector conservation requirement. Green's function calculations have shown an energy broadening of $\sim$10 meV due to the N-center scattering at the edge of the lower subband for $GaAs_{0.95}N_{0.05}$ alloys.[17] The N-induced relaxation of the **k**-vector conservation also leads to an intraband scattering within the lowest conduction subband. As is seen in Fig. 2,

the measured PL peak energy makes a smooth transition between the low- and high-pressure regimes, rather than showing a kink as on the calculated curves. This fact suggests a strong mixing between the $E_{N\Gamma-}$ and E_{NX-} conduction-band minima when they are degenerate in energy. The best agreement with the data, as denoted by solid lines, was obtained by using the previously determined[6] coupling constant $C_{N\Gamma} = 3.05$ eV at the Γ point and setting $C_{NX} = 0.90$ eV for the coupling constant at the Brillouin-zone edge. The energy of the N localized state was set to be at $E_N \sim 2.15$ eV with a small pressure dependence of 1.2 meV/kbar. This energy location and pressure dependence are consistent with the average values for the variety of bound exciton lines in dilute N-doped GaP observed in previous reports.[18] Although X states could be expected to be more concentrated than Γ states on the group V sites (which N substitutes), the X-N coupling is much weaker than the Γ-N coupling. As pointed out in Ref. 19, this is partly because X states are essentially antibonding p-like, while Γ states are s-like with the same A_1 symmetry as the N localized state has.

Evidence of similar off-zone-center coupling in the $GaAs_{1-x}N_x$ alloy has been observed by Seong, Mascarenhas, and Geisz using resonant Raman scattering[20] and by Perkins *et al.* using the electroreflectance technique.[21] In these ambient-pressure experiments, a coupling between E_N and the conduction-band edge E_L at the L point of the Brillouin zone was observed. This is because in GaAs, the E_N level is closer to the L band minima ($E_L - E_N = 0.12$ eV) than to the X minima ($E_X - E_N = 0.27$ eV), whereas in GaP E_N is located much closer to the X band minima than to the L minima, $E_X - E_N = 0.17$ eV and $E_L - E_N = 0.46$ eV. In GaAs, the negative pressure derivative resulting from the coupling between E_N levels and E_X minima can be observed only at very large pressures when the X band minima shift down to the band edge. In fact, the onset of this effect has been observed in $GaAs_{1-x}N_x$ at a pressure of about 120 kbars.[10] Shown in Fig. 3 is a schematic diagram of the conduction band of $GaP_{0.977}N_{0.023}$ at ambient pressure. The hybridization parameter $C_{NM}(k)$ is essentially the Fourier transform of the interaction matrix element between the localized impurity state and the Wannier function of the band.[22] Due to the localized nature of these two wave functions, the matrix element is a spatially rapidly decaying function. In the calculation of Fig. 3, $C_{NM}(k)$ is thus assumed to take the functional form of the Fourier transform of an exponentially decaying function expressed as[17]

$$C_{NM}(k) = \frac{C_{N\Gamma}}{[1+(ak)^2]^2}. \qquad (2)$$

In Eq. (2), a is a parameter to describe the spatial extent of the N localization wave function, and is estimated to be of the order of the lattice constant of the host, so that C_{NX} agrees with the value determined from the N-X anticrossing fitting. The energy minima restructured from the Γ-N and X-N anticrossing interactions at 100 kbars are also shown in symbols. The fundamental band gap of the material switches from direct at ambient pressure to indirect at high pressures.

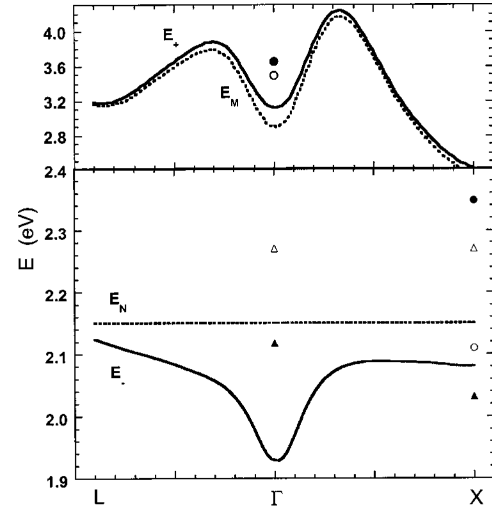

FIG. 3. Band anticrossing induced restructuring of the conduction band of $GaP_{1-x}N_x$. The curves show the lower $E_-(k)$ and the upper $E_+(k)$ band edges at ambient pressure. The symbols show the energy minima at 100 kbar: open triangles, E_N; open circles, E_M (including E_Γ and E_X); solid triangles, E_- (including $E_{N\Gamma-}$ and E_{NX-}); solid circles, E_+ (including $E_{N\Gamma+}$ and E_{NX+}). Note the change in the nature of the lowest conduction-band edge, from direct at ambient pressure to indirect, mostly X-like at 100 kbar.

Figure 4 shows the ambient-pressure band-gap energy of four samples with different N concentrations measured using PL at 30 K. The lowest solid line represents the N-like conduction-band minimum of $GaP_{1-x}N_x$ restructured through the interaction between $|N\rangle$ and $|\Gamma\rangle$ as calculated from Eq. (1). Also shown in solid lines are the predicted energies of the other minimum restructured from the interaction between $|N\rangle$ and the X band, and two higher energies corresponding to the X-like and Γ-like edges of the upper subbands calculated from Eq. (1). These higher critical energies may be observed by modulation spectroscopy.

In summary, we have performed photoluminescence measurements of $GaP_{1-x}N_x$ alloys at 30 K. Based on the nonmonotonic pressure dependence of the PL peak energy, it is

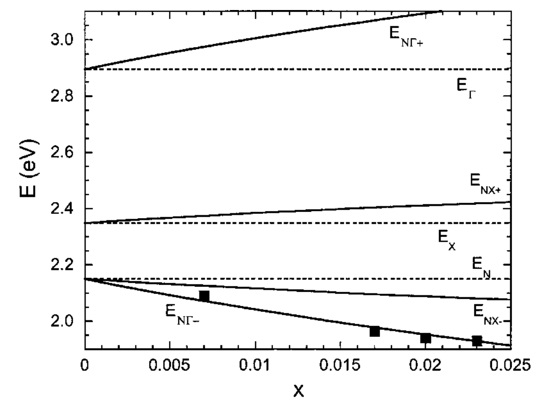

FIG. 4. PL peak energy at 30 K and ambient pressure as a function of N concentration. The dashed lines mark the energy locations of the N state, the Γ band, and the X band minima of GaP. The solid lines are the energies of the subbands edges as a result of the band anticrossing repulsion.

demonstrated that the fundamental band gap in $GaP_{1-x}N_x$ changes its nature from direct to indirect at high pressures. The anticrossing repulsion between the N localized state and the X conduction minima of the host GaP is proposed to explain the negative pressure dependence of the fundamental band gap at high pressures. The coupling between the N localized state and the Γ band state is more than three times stronger than the coupling between the N localized state and the X band state. This finding accounts for a number of previous observations indicating that the off-zone-center minima are affected only when their energies lie close to the localized N-level energy.

The work at the Lawrence Berkeley National Lab is part of the project on the "Photovoltaic Materials Focus Area" in the DOE Center of Excellence for the Synthesis and Processing of Advanced Materials, and was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The work at UCSD is partially supported by a UC MICRO program with Rockwell International and the DARPA Heterogeneous Optoelectronics Technology Center. The work at UCSD is partly supported by the National Renewable Energy Laboratory (AAD-9-18668-07).

*Electronic address: jqwu@socrates.berkeley.edu

†Electronic address: w_walukiewicz@lbl.gov

[1] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys., Part 2 **31**, L853 (1992).

[2] J. Neugebauer and C. Van de Walle, Phys. Rev. B **51**, 10 568 (1995).

[3] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).

[4] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).

[5] J. D. Perkins, A. Mascarenhas, Y. Zhang, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 3312 (1999).

[6] W. Shan, W. Walukiewicz, K. M. Yu, J. Wu, J. W. Ager III, E. E. Haller, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **76**, 3251 (2000).

[7] H. P. Xin, R. J. Welty, and C. W. Tu, IEEE Photonics Technol. Lett. **12**, 960 (2000); M. Kondow, S. Nakatsuka, T. Kitatani, Y. Yazawa, and M. Okai, Jpn. J. Appl. Phys., Part 1 **35**, 5711 (1996).

[8] J. F. Geisz, D. J. Friedman, J. M. Olson, S. R. Kurtz, and B. M. Keyes, J. Cryst. Growth **195**, 401 (1998).

[9] E. D. Jones, N. A. Modine, A. A. Allerman, S. R. Kurtz, A. F. Wright, S. T. Tozer, and X. Wei, Phys. Rev. B **60**, 4430 (1999); T. Mattila, S. H. Wei, and A. Zunger, *ibid.* **60**, R11 245 (1999); M. Kozhevnikov, V. Narayanamurti, C. V. Reddy, H. P. Xin, C. W. Tu, A. Mascarenhas, and Y. Zhang, *ibid.* **61**, R7861 (2000).

[10] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and Sarah R. Kurtz, J. Appl. Phys. **86**, 2349 (1999).

[11] A. N. Kocharyan, Sov. Phys. Solid State **28**, 6 (1986); M. A. Ivanov and Yu. G. Pogorelov, Sov. Phys. JETP **49**, 510 (1979); **61**, 1033 (1985).

[12] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966); D. J. Wolford, J. A. Bradley, K. Fry, and J. Thompson, in *Physics of Semiconductors*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1984).

[13] H. P. Xin, C. W. Tu, Y. Zhang, and A. Mascarenhas, Appl. Phys. Lett. **76**, 1267 (2000).

[14] M. B. Panish and H. C. Casey, J. Appl. Phys. **40**, 163 (1969).

[15] S. Ves, K. Stossner, C. K. Kim, and M. Cardona, Solid State Commun. **55**, 327 (1985).

[16] T. Takizawa, J. Phys. Soc. Jpn. **52**, 1057 (1983).

[17] J. Wu, W. Walukiewicz, and E. E. Haller, Phys. Rev. B (to be published).

[18] J. N. Baillargeon, K. Y. Cheng, G. E. Hofler, P. J. Pearah, and K. C. Hsieh, Appl. Phys. Lett. **60**, 2540 (1992); B. Gil, M. Baj, J. Camassel, H. Mathieu, C. Benoit a la Guillaume, N. Mestres, and J. Pascual, Phys. Rev. B **29**, 3398 (1984).

[19] Bernard Gil, Solid State Commun. **114**, 623 (2000).

[20] M. J. Seong, A. Mascarenhas, and J. F. Geisz, Appl. Phys. Lett. **79**, 1297 (2001).

[21] J. D. Perkins, A. Mascarenhas, J. F. Geisz, and D. J. Friedman, Phys. Rev. B **64**, 121301 (2001).

[22] P. W. Anderson, Phys. Rev. **124**, 41 (1961).