Band Anticrossing in GaP$_{1-x}$N$_x$ Alloys

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The optical properties of GaP$_{1-x}$N$_x$ alloys (0.7% $\leq x \leq$ 2.3%) grown by gas-source molecular-beam epitaxy have been studied using photoluminescence spectroscopy under hydrostatic pressures up to 133 kbar at 30K. The peak energy of the band edge photoluminescence spectrum shows an unusual, non-monotonic 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.

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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 one percent N for As in GaAs reduces the band gap by more than 0.18eV [1-5]. The alloying of GaP with less than one percent 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 [9-11]. We have shown previously that the electronic structure of group III-N-V alloys can be quantitatively described by an 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 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 [11]. The interaction strength, represented by a parameter $C_{N\Gamma}$, has been determined to be 2.7 eV 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 wavefunction 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 IIIV$_{1-x}$N$_x$ alloys. In this letter 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 dependency 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 0.2μm 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 [12].

The samples were mechanically polished into small chips of ~100×100 μm^2 in size and a thickness of ~10 μm, and mounted into gasketed diamond anvil cells for the application of hydrostatic pressure. The applied pressure was calibrated by the standard method of monitoring the red shift of the ruby R1 line. Photoluminescence (PL) signals were generated in the backscattering geometry by excitation with the 476.5 nm line of an argon laser and were dispersed by a 1m 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 35kbar for x=1.3%). Cooling down the sample greatly improves the luminescence efficiency. Shown in Fig.1(a) is the 30K 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.

Fig.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 ~ 80±10 kbar, the pressure at which 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. It should be noted that N-free GaP did not show a detectable PL signal under the same experimental conditions. All three N-containing samples show a similar non-monotonic 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 160meV at ambient pressure to 50meV at ~110kbar. As is well known, in GaP the X band minimum (E_X) is located at ~ 2.35eV above the valence band edge at ambient pressure at 30K [13], and has a negative pressure coefficient of about -0.0024eV/kbar [14]. 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],

$$E_\pm(k) = \frac{1}{2}\left\{[E_M(k) + E_N] \pm \sqrt{[E_M(k) - E_N]^2 + 4C_{NM}^2(k) \cdot x}\right\}, \tag{1}$$

where $E_M(k)$ is the energy dispersion of the lowest conduction band of the host GaP, and E_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_{NM} and is assumed to be k-dependent.

The location of E_Γ in GaP as function of the hydrostatic pressure is well known and can be written as $E_\Gamma(p) = 2.9 + 0.0097p - 3.5 \times 10^{-5} p^2$ [14, 15], where $E_\Gamma(p)$ is measured in eV and p is the hydrostatic pressure in kbar. 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 $E_{N\Gamma-}$, which evolves from the E_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

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to that of E_N level. At higher pressures the E_X edge shifts downwards, and the E_{NX-} edge resulting from the anticrossing interaction between E_X and E_N becomes the lowest conduction band edge. The indirect transitions from E_{NX-} 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 wavevector conservation requirement. Green's function calculations have shown an energy broadening of ~10meV due to the N-center scattering at the edge of the lower subband for $GaAs_{0.95}N_{0.05}$ alloys [16]. The N-induced relaxation of the **k**-vector conservation also leads to an intraband scattering within the lowest conduction subband. Thus as is seen in Fig.2, the fact that the measured PL peak energy makes a smooth transition between the low and high pressure regimes, 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 $C_{N\Gamma}$=3.05eV at the Γ point and and setting C_{NX}=0.90eV 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. 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.[17], 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 $GaAs_{1-x}N_x$ alloy has been observed by Seong *et.al.* using resonant Raman scattering [18] and by Perkins *et.al.* using the electroreflectance technique [19]. In these ambient-pressure experiments, a coupling between E_N and the conduction band edge E_L at 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 kbar [10]. Shown in Fig.3 is a schematic diagram of the conduction band of GaP$_{0.977}$N$_{0.023}$ at ambient pressure. In the calculation, $C_{NM}(k)$ is assumed to take the functional form of the Fourier transform of an exponentially decaying function, expressedly [16],

$$C_{NM}(k) = \frac{C_{N\Gamma}}{\left[1 + (a\,k)^2\right]^2}. \tag{2}$$

In Eq.(2), a is a parameter to describe the spatial extend of the N localization wavefunction, 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 kbar are also shown in symbols. The fundamental band gap of the material switches from direct at ambient pressure to indirect at high pressures.

Fig.4 shows the ambient-pressure band gap energy of four samples with different N concentrations measured using PL at 30K. 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 energy 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 30K. Based on the non-monotonic pressure dependence of the PL peak energy, it is 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.

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Figure Captions

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=30K. (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.

Fig.2. PL peak energy at 30K 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. Note the different scale for the upper portion of the plot.

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 100kbar: 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.

Fig.4. PL peak energy at 30K 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.
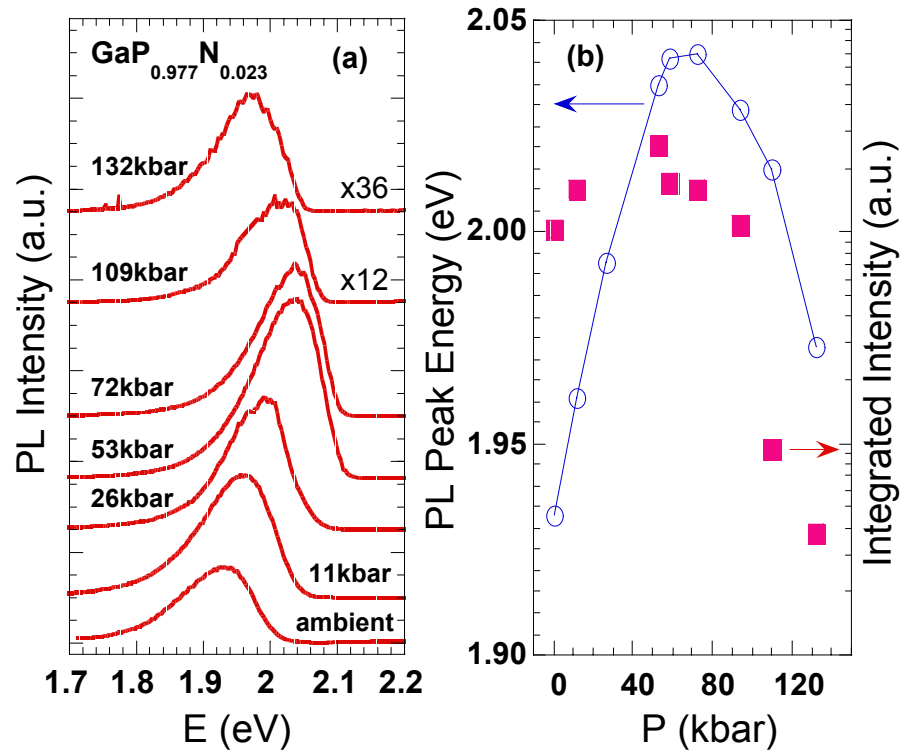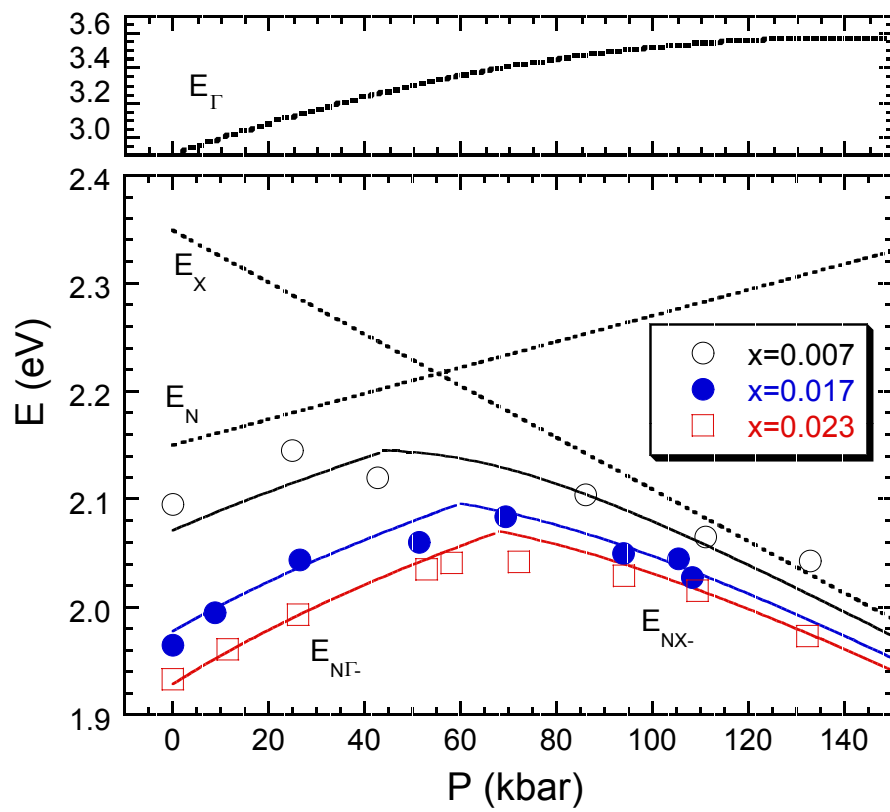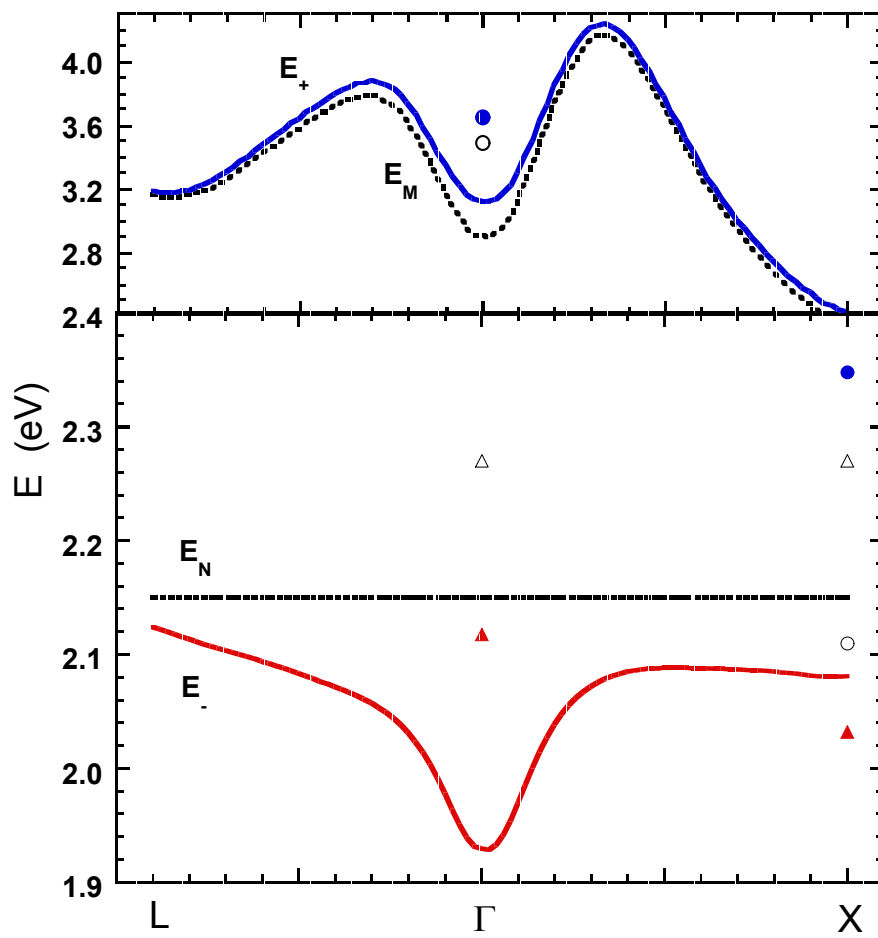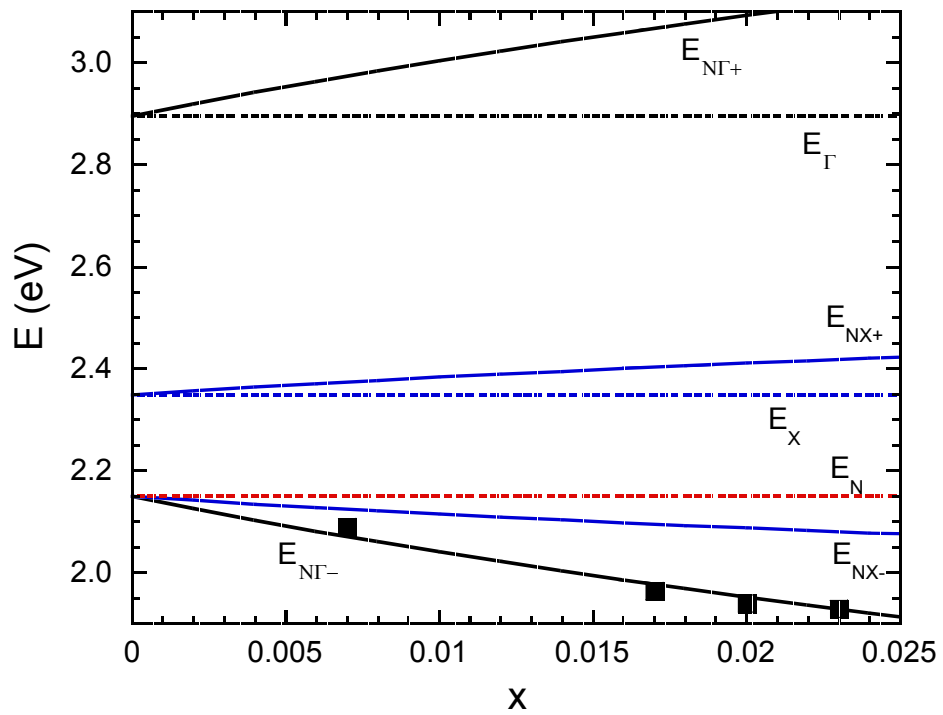
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