Band Anticrossing in GaInNAs Alloys

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We present evidence for a strong interaction between the conduction band and a narrow resonant band formed by nitrogen states in $Ga_{1-x}In_xN_yAs_{1-y}$ alloys. The interaction leads to a splitting of the conduction band into two subbands and a reduction of the fundamental band gap. An anticrossing of the extended states of the conduction band of the $Ga_{1-x}In_xAs$ matrix and the localized nitrogen resonant states is used to model the interaction. Optical transitions associated with the energy minima of the two subbands and the characteristic anticrossing behavior of the transitions under applied hydrostatic pressure have been unambiguously observed using photomodulation spectroscopy. The experimental results are in excellent quantitative agreement with the model. [S0031-9007(98)08364-1]

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Semiconductor alloys containing component elements with distinctly different properties are currently attracting significant attention. In particular, intensive experimental [1–7] and theoretical [8–12] efforts have recently been directed towards developing an understanding of the properties of group III-N-V alloys in which the group-V element is partially replaced by nitrogen. It has been found that incorporating low concentrations of N has a profound effect on the electronic properties of these materials. A reduction of the band gap exceeding 0.1 eV per atomic percent of N content was observed in GaN_xAs_{1-x} for $x < 0.015$ [1]. This discovery has opened an interesting possibility of using N containing alloys for long wavelength optoelectronic devices [13]. It also raises an important question as to the mechanism responsible for this unusual behavior. Model calculations of the band structure of some of the group III-N-V alloys have shown that the reduction of the band gap is due to the highly localized nature of the perturbation introduced by N atoms [8–12,14]. The largest contributions to the band gap reduction originate from structural relaxation and charge exchange that are, respectively, proportional to the differences in the atomic orbital size and energy of the As and N atoms [8,11].

It is well known that at very low concentrations N introduces a highly localized acceptorlike level in conventional III-V compound semiconductors. In GaP the level is located slightly below the conduction band minimum. Extrapolation of the data obtained for GaAsP alloys suggests the level is located at about 0.3 eV above the bottom of the conduction band in GaAs [15]. This has been confirmed by measurements of hydrostatic pressure dependent photoluminescence spectra that have shown an emergence of N bound excitons at a pressure of about 2.3 GPa [16,17].

In this Letter, we show that the incorporation of N into GaInAs alloys leads to a strong interaction between the conduction band and a narrow resonant band formed by the N states due to the highly localized nature of the perturbation introduced by N atoms, resulting in a splitting of the conduction band and a reduction of the fundamental band gap. This is supported by the unambiguous observations of the optical transitions associated with the two branches of the split lowest conduction band in $Ga_{1-x}In_xN_yAs_{1-y}$ alloy samples with different In and N concentrations and a characteristic anticrossing behavior of the two branches under hydrostatic pressure. The observed reduction of the band gap energy of $Ga_{1-x}In_xN_yAs_{1-y}$ alloys with small N concentration can be fully explained by this interaction.

The $Ga_{1-x}In_xN_yAs_{1-y}$ epitaxial layers used in this work were grown on GaAs substrates by metalorganic vapor phase epitaxy using dimethylhydrazine as the nitrogen source. Layers were grown at 5 μm/h and 570–580 °C. The layer thicknesses vary from 0.5 to 5.0 μm. The nitrogen content of the samples was determined using reflection (004) double-crystal x-ray diffraction measurements [18].

To measure the band gap energy of the $Ga_{1-x}In_xN_yAs_{1-y}$ samples under hydrostatic pressure, photomodulation spectroscopic measurements were carried out in either transmission or reflection geometry at room temperature (295 K). Photomodulation spectroscopy is a differential method probing the variation of the absorptivity of the samples caused by the modulation of physical parameters such as the built-in surface field in the system [19]. The resulting spectra are characterized by features arising from direct interband transitions at high symmetry points in the band structure [19,20]. 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 (4420 Å) provided the photomodulation. The photomodulated transmission signals were detected by a Ge or Si photodiode using a phase-sensitive lock-in amplification system. Application of pressure was accomplished by mounting small sample chips with sizes of $\sim 200 \times 200\ \mu m^2$ into gasketed diamond anvil cells.

Figure 1 shows the pressure dependence of the fundamental band gaps of a few $Ga_{1-x}In_xN_yAs_{1-y}$ samples. The band gap energies were determined by photomodulated transmission (PT) measurements. In the case of $Ga_{0.92}In_{0.08}As$ ($y = 0$), the band gap increases linearly with applied hydrostatic pressure at a rate of ~ 100 meV/GPa. This type of behavior is commonly observed for conventional group III-V semiconductors. Adding N completely changes the pressure dependence. All the $Ga_{1-x}In_xN_yAs_{1-y}$ samples exhibit a much weaker dependence of the band gap energy at low pressures and a tendency of the energy gap to saturate at high pressures. The saturation is clearly visible in the samples with lower N contents. The pronounced change in the pressure dependence of the energy gap can be understood in terms of a pressure-induced transformation of the nature of the lowest conduction band states, namely, from extended to highly localized. The gradual nature of the transformation, shown in Fig. 1, indicates that it cannot be associated with a pressure-induced crossover of noninteracting Γ and X conduction band valleys, but rather suggests that it is a manifestation of an anticrossing behavior of two strongly interacting energy levels with distinctly different pressure dependencies. The possibility of the Γ-X crossing smear out due to a strong impurity-induced Γ-X interaction can be ruled out. If this were the case, the pressure dependence of the fundamental band gap for the $Ga_{1-x}In_xN_yAs_{1-y}$ samples shown in Fig. 1 should be similarly independent of the N content in the low pressure region when the Γ point energy is located well below the X conduction band edges.

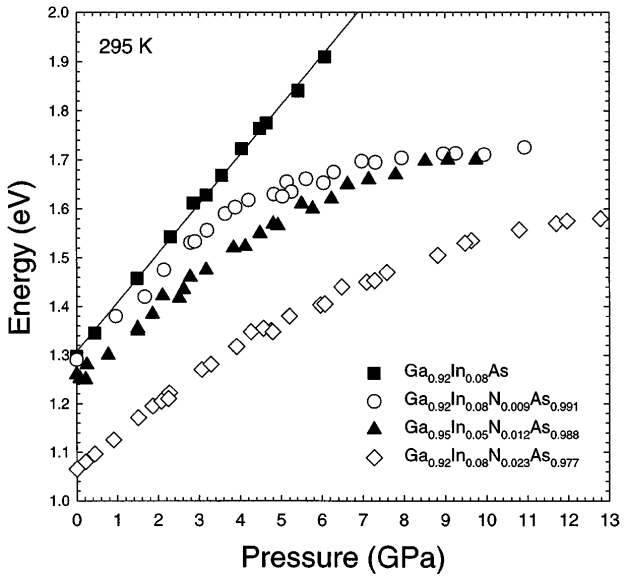

FIG. 1. Change of the fundamental band gaps of different $Ga_{1-x}In_xN_yAs_{1-y}$ samples as a function of hydrostatic pressure. The solid line is a best linear fit to the experimental data obtained from the $Ga_{0.92}In_{0.08}As$ sample.

In order to explain the observed pressure dependence, we consider a simple model of two interacting energy levels: one associated with extended states of the GaInAs matrix and the other with the localized N states. Following standard procedures we assume that the interaction of the two types of states can be treated as a perturbation which leads to the following eigenvalue problem:

$$\begin{vmatrix} E - E_M & V_{MN} \\ V_{MN} & E - E_N \end{vmatrix} = 0\,, \tag{1}$$

where E_M and E_N are the energies of the GaInAs matrix conduction band edge and of the N level relative to the top of the valence band, respectively, and V_{MN} is the matrix element describing the interaction between those two types of states. Incorporation of the interaction represented by the matrix element V_{MN} leads to a mixing and anticrossing of these states. The two solutions of the problem can be written as

$$E_{\pm} = (E_N + E_M \pm [(E_N - E_M)^2 + 4V_{MN}^2]^{1/2})/2\,. \tag{2}$$

To simplify the case without involving too many unknown parameters, we begin by assuming that the nitrogen level $E_N = 1.74$ eV and is insensitive to applied pressure. (Later we show that its pressure dependence is fairly weak.) For $In_{0.08}Ga_{0.92}As$, as shown in Fig. 1, the pressure dependence of the conduction band edge E_M is given by

$$E_M = 1.30 + 0.1P\ (\text{eV})\,, \tag{3}$$

where E_M is measured with respect to the valence band edge, and P is the hydrostatic pressure in units of GPa. Using Eqs. (2) and (3), we find that E_M crosses E_N at 4.1 GPa. As shown in Fig. 2, the lower branch solution E_- given by Eq. (2) can fit the pressure dependence of the experimentally observed band gap energies in $In_{0.08}Ga_{0.92}N_xAs_{1-x}$ very well. As expected, the strength of the coupling V_{MN} increases with the nitrogen composition. It changes from $V_{MN} = 0.12$ eV for $x = 0.009$ to 0.4 eV for $x = 0.023$. The downward shift of the lower branch E_- can account well for the reduction of the fundamental band gap observed in $Ga_{1-x}In_xN_yAs_{1-y}$ alloys. This demonstrates that the interaction between extended band states and localized N states is responsible for the downward shift of the conduction band edge.

A very important inference of our model is that it predicts a splitting of the conduction band into two subbands with the energy minimum at E_- and E_+. In search of the predicted splitting, we performed photomodulated reflectance (PR) measurements over a wide spectral range. Figure 3 shows PR spectra taken at atmospheric pressure

from a $Ga_{0.92}In_{0.08}As$ and two $Ga_{1-x}In_xN_yAs_{1-y}$ samples. The ternary alloy sample (without nitrogen) exhibits, as commonly observed in most direct band gap semiconductors, two sharp derivativelike spectral signatures in its PR spectrum corresponding to the transition from the top of the valence band to the bottom of the conduction band (E_0 transition), and the transition between the spin-orbit split-off band and the conduction band minimum ($E_0 + \Delta_0$ transition). The doubletlike spectral structure of E_0 transition is due to a well-known strain effect in which the lattice mismatch between the $Ga_{0.92}In_{0.08}As$ epilayer and GaAs substrate induces a compressive strain resulting in the lifting of degeneracy of the heavy-hole and light-hole valence bands at the center of the Brillouin zone.

For the quaternary samples, in addition to the spectral features related to the transition across the fundamental band gap (E_- transition) and the transition from the top of the spin-orbit split-off valence band to the bottom of the conduction band ($E_- + \Delta_0$ transition), an extra feature (E_+) appears on a higher energy side in the PR spectra. While the E_- and $E_- + \Delta_0$ transitions shift to lower energy with increasing In and N concentrations, the E_+ transition moves in the opposite direction. This demonstrates that the splitting between E_- and E_+ increases with N content, as described by Eq. (2). It is important to note that the spin-orbit splitting energy Δ_0 is equal to $\sim$0.34 eV for all measured samples and does not depend on N content. The results demonstrate that incorporation of N into GaInAs affects mostly the conduction band and has a negligible effect on the electronic structure of the valence band.

To further demonstrate the band anticrossing, as predicted by our model, we show the experimentally measured energy positions of the E_- and E_+ transitions in the $Ga_{0.95}In_{0.05}N_{0.012}As_{0.988}$ sample as a function of applied hydrostatic pressure in Fig. 4, along with the pressure dependence of these two branches calculated from Eq. (2). The inset shows a representative PR spectrum under pressure. It can be readily observed that the E_- and E_+ transitions exhibit a classical anticrossing behavior. The calculations are in excellent agreement with the experimental results for $V_{MN} = 0.2$ eV. We found that the best agreement was obtained for E_N slightly dependent on pressure. Our results yield $E_N = 1.65$ eV with a pressure dependence of 15 meV/GPa. The obtained pressure coefficient for the N level is consistent with the results of pressure dependent photoluminescence measurements in GaAs:N [16,17].

The results in Fig. 4 show that application of high pressure gradually changes the character of the E_- branch from extended E_M-like to localized E_N-like and the character of the E_+ branch from localizedlike to extendedlike. Since the dipole interaction for optical transitions couples much more strongly to extended states than to the localized states, it is expected that the pressure-induced change in the character of the conduction subband wave functions will be reflected in the intensity of the optical transitions from the valence band to the E_- and E_+ subbands. Indeed we

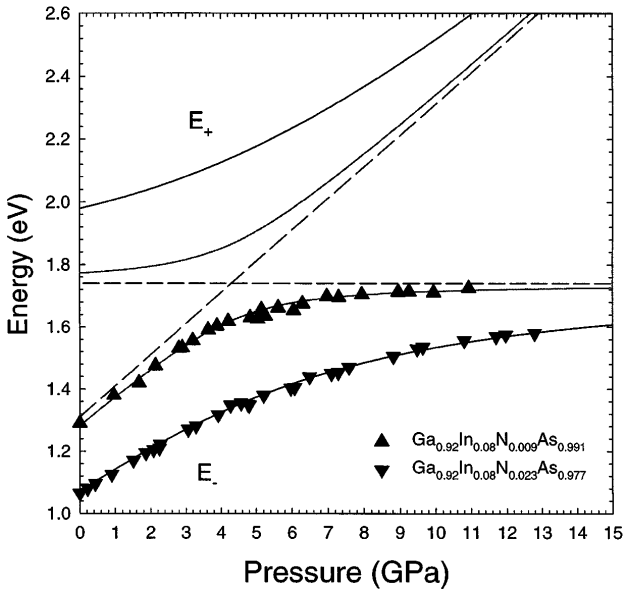

FIG. 2. A comparison of the experimental results with model calculations (solid lines) for the band anticrossing in $Ga_{0.92}In_{0.08}N_yAs_{1-y}$. Also shown are the positions of unperturbed E_M and E_N levels (dashed lines).

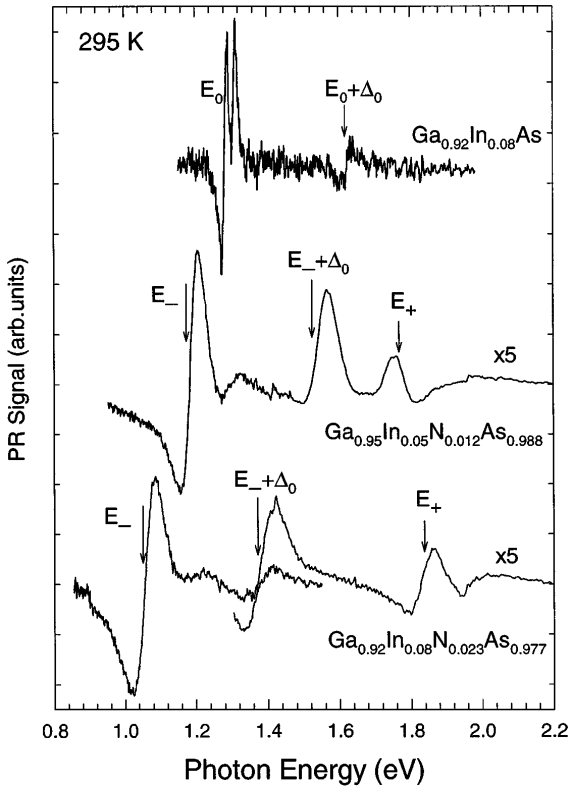

FIG. 3. PR spectra of $Ga_{1-x}In_xN_yAs_{1-y}$ samples: (top) $Ga_{0.92}In_{0.08}As$ ($y = 0$), the E_0 and $E_0 + \Delta_0$ transitions are observed; (middle) $Ga_{0.95}In_{0.05}N_{0.012}As_{0.988}$, the E_- and $E_- + \Delta_0$ transitions shift to lower energy, and a new feature E_+ appears; (bottom) $Ga_{0.92}In_{0.08}N_{0.023}As_{0.977}$ (this sample has the same In content as the top sample), the addition of more N pushes the E_- and $E_- + \Delta_0$ to lower energy and E_+ to higher energy. The arrows indicate the transition energy positions.

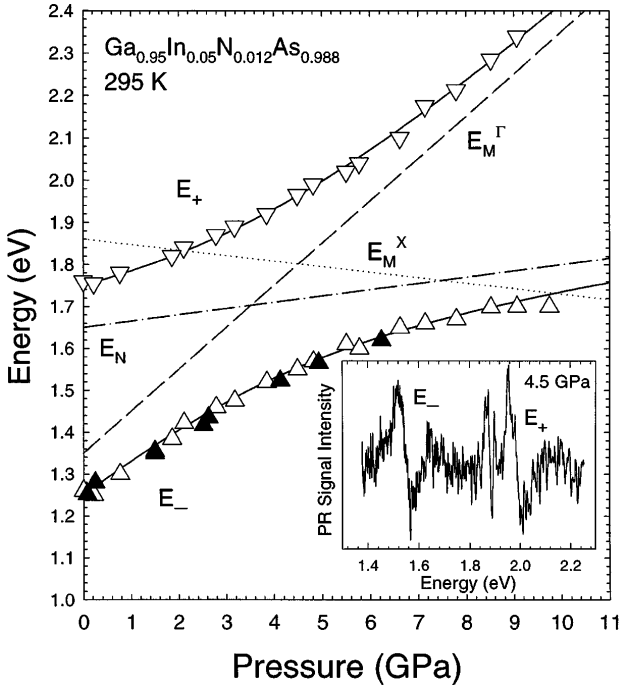

FIG. 4. Change of the E_- and E_+ transition energies in $Ga_{0.95}In_{0.05}N_{0.012}As_{0.988}$ as a function of applied pressure. The open triangles are PR data and the filled triangles are PT data. The solid lines are model calculation results for the band anticrossing. The dashed, dotted, and dot-dashed lines are the pressure dependence of the Γ and X conduction band edges of the $Ga_{0.95}In_{0.05}As$ matrix and the N level relative to the top of the valence band, respectively. The inset shows a PR spectrum taken at 4.5 GPa. The narrow PR spectral feature at energy below E_+ originates from the GaAs substrate.

observed a gradual increase of the intensity ratio of the PR signals associated with the E_+ and E_- transitions. While the signal intensity of the PR spectral feature related to the E_+ transition is at least an order of magnitude smaller than that of the E_- transitions at atmospheric pressure (see Fig. 3), the intensity of the E_+ transition has, in fact, become stronger than that of the E_- transition at 4.5 GPa, as shown in the inset of Fig. 4. The observed results are once again consistent with our model which predicts an equal intensity for both transitions when E_M crosses over E_N at a pressure around 3.5 GPa.

In conclusion, we have discovered an anticrossing induced conduction band splitting caused by the strong interaction between the extended conduction band states and localized N resonant states in $Ga_{1-x}In_xN_yAs_{1-y}$ alloys. The splitting of the conduction band into two subbands and a characteristic band anticrossing behavior have been experimentally observed using photomodulation spectroscopy in conjunction with large hydrostatic pressure. Our results indicate that the interaction is fully responsible for the observed N-induced redshift of the fundamental band gap in the GaInNAs alloy system for small nitrogen concentrations.

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