Band anticrossing in InGaPN alloys induced by N-related localized states

K. I. Lin and J. S. Hwang

Department of Physics, National Cheng Kung University, Tainan 701, Taiwan

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Temperature-dependent photoreflectance measurements are employed to characterize the electronic band structure of InGaPN grown on GaAs substrates. In addition to the fundamental band gap, the upper subband \( E_x \) is observed as predicted by the band anticrossing (BAC) model. By eliminating the contributions of the epitaxial-strain and atomic-ordering effects in InGaPN and also assigning the localized state energy \( E_N \) introduced by an isolated N to be 2.040 eV at 293 K, the interaction potential \( V \) is determined as 1.449±0.170 eV. The incorporation of a temperature-dependent \( E_N \) level into the BAC model fits the experimental data better than assuming \( E_N \) to be a constant. This contrasts with previously published results and so provides a different view of the temperature dependence of the \( E_N \) level in InGaPN. © 2006 American Institute of Physics. [DOI: 10.1063/1.2387972]

For conventional III-V alloys, such as In\(_{x}\)Ga\(_{1-x}\)As, the deviation of the band gap energy from that of a composition-weighted linear average is usually small and well described by the quadratic correction, \( \Delta E_g(x) = bx(x-1) \), where \( b \) is the bowing coefficient. However, incorporation of small amounts of nitrogen into conventional III-V semiconductors causes a profound reduction of the fundamental band gap energy, which results in a large composition-dependent bowing coefficient.\(^1\) This means that the type of bowing discussed above does not adequately describe the dilute nitrides, such as the Ga\(_{1-x}\)As\(_{1-y}\)N\(_y\), \(^2\) Ga\(_{1-x}\)P\(_{1-y}\)N\(_y\), \(^3\) and In\(_{1-x}\)Ga\(_{1-y}\)As\(_{1-y}\)N\(_y\) alloys, \(^4\) which have recently attracted considerable attention. The band anticrossing (BAC) model is introduced to describe the influence of N incorporation on the band structure of the dilute nitrides.\(^2\)\(^-\)\(^6\) An isolated N introduces highly localized states in these nitrides, which interact with the extended conduction-band states of the host semiconductor matrix. The interaction splits the conduction band into two subbands defined as the upper subband \( E_x \) and the lower subband \( E_N \) which corresponds to the conduction-band edge. More recently, dilute nitride alloys, i.e., In\(_{1-x}\)Ga\(_x\)P\(_{1-y}\)N\(_y\), have been grown by gas source molecular beam epitaxy on GaAs substrates. There are published reports of the band-gap reduction in InGaPN analyzed by the bowing coefficient or the BAC model,\(^5\)\(^7\) but no experimental observations of the upper subband \( E_x \) have been reported to date.

In this letter, the fundamental band gap (\( E_0 \) or \( E_x \) transition) and the \( E_x \) transition of In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_y\) are obtained from photoreflectance (PR) spectra measured at various temperatures. The BAC model is used to estimate the dependence of the energy position of the lower and upper subbands on the N content. Eliminating the contributions of the epitaxial-strain and atomic-ordering effects in InGaPN,\(^8\) the corresponding BAC parameters are determined. Additionally, the temperature dependence of the band gap is described by the BAC model incorporating two \( E_N \) level parameters, one temperature dependent and the other a constant. In our hands, this assumption of the temperature dependent \( E_N \) level results in a better fit with the experimental data in contrast to a recent report.\(^5\)

The In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_y\)/GaAs heterostructures are grown on a (001) GaAs semi-insulating substrate by gas source molecular beam epitaxy. The growth sequence involves the growth of a 0.5 \( \mu \)m thick undoped In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_y \) (\( y = 0 \), 0.005, 0.010, and 0.020) layer on a 0.2 \( \mu \)m thick GaAs buffer layer. The growth temperature is maintained at approximately 420 °C, with nitrogen plasma ignited. A standard arrangement of the photoreflectance apparatus is used.\(^9\) The 325 nm line of a He–Cd laser serves as the pumping beam. The PR measurements are performed in a closed cryostat at temperatures ranging from 25 to 300 K.

Assuming that N-related localized states are only weakly coupled to the extended states of the host semiconductor matrix, the BAC model yields the following equation for the two coupled bands at \( \Gamma \) point:

\[
E_x = \frac{1}{2} (E_N + E_{\Gamma}) \pm \sqrt{(E_N - E_{\Gamma})^2 + 4V^2},
\]

where \( E_{\Gamma} \) and \( E_N \) represent the energies, relative to the top of the valence band, of the unperturbed conduction band and of the localized states, respectively, \( V \) is the interaction potential between the two bands, and \( y \) is the N content. The interaction of the conduction-band edge with the dispersionless N level results in a splitting of the conduction band into two subbands, \( E_x \) and \( E_{\Gamma} \). The downward shift of the lower \( E_x \) subband is responsible for the band-gap reduction. Figure 1 depicts the PR spectra measured from several In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_y\) samples at 293 K. The spectra with energy higher than the vertical dotted lines are twice or threefold enlarged for clarity. The line shape of the PR spectrum is fitted to:

\[
\Delta R/R = Re[\alpha e^{\theta (E - E_j + i\Gamma)^{-m}}],
\]

where \( E \) is the photon energy and \( \alpha, \theta, E_j, \) and \( \Gamma \) are the amplitude, phase factor, transition energy, and broadening parameter, respectively. The parameter \( m \) depends on the dimensionality of the critical point. Here, \( m = 2.5 \) is used, corresponding to a three-dimensional critical point. In the spectrum with \( y = 0 \), the \( E_0 \) transition indicates the fundamental band gap of InGaP. In the spectra with \( y > 0 \), the \( E_{\Gamma} \) transi-
FIG. 1. PR spectra measured from In$_{\text{x}}$Ga$_{\text{1-x}}$P$_{0.995}$N$_{0.005}$, samples at 293 K. The open circles for the y=0.0% spectrum represent the theoretical fit using Eq. (2). The spectra with energy higher than the vertical dotted lines are enlarged to show greater detail. The dotted arrows indicate the $E_y$ transition energy predicted by the BAC model.

The features observed from the back-folded conduction band induced by ordering, $E_y$ transitions from the valence band to the conduction band can be expressed as:

$$E_y(\eta, e_{\perp}) = E_{g}(0,0) + \eta^2 \Delta E_{g}(1,0) + \frac{1}{3} [\Delta SO + \eta^2 \Delta^O_{111}(1)]$$

$$+ \frac{2\alpha(C_{111} - C_{12})}{C_{11}} e_{\perp} \cdot e_{\perp},$$

(3)

where $\eta$ is the order parameter, $e_{\perp}$ is the biaxial strain component, $E_{g}(0,0)$, the band gap of the strain-free and perfectly random In$_{\text{x}}$Ga$_{\text{1-x}}$P$_{0.995}$N$_{0.005}$, $\Delta E_{g}(1,0)$, the band-gap reduction due to ordering, $= -0.471$ eV, $\Delta SO$, the spin-orbit splitting, $= 0.10$ eV, $\Delta^O_{111}(1)$, the fully ordered crystal field splitting, $= 0.20$ eV, $\alpha$ is the hydrostatic deformation potential, and $C_{11}$ and $C_{12}$ are the elastic constants. The values of $\alpha$, $C_{111}$, and $C_{12}$ of InGaP are derived from the linear interpolation of the known values for InP, GaP, cubic GaN, and cubic InN. By substituting the values of $\eta$ and $e_{\perp}$ reported in Ref. 8 into Eq. (3), the conduction bands are obtained as 1.875, 1.863, 1.830, and 1.793 eV for $y=0-0.020$. Hence, the band gaps $E_{g}$ including the strain and ordering effects are 1.826, 1.813, 1.779, and 1.738 eV for $y=0-0.020$ and are plotted as open circles in Fig. 2. The band gap $E_{g}$ of InGaP agrees well with the band gap $E_{g}$ obtained by the PR measurement. As a simplification, the band gaps $E_{g}$ are fitted to a linear function of nitrogen content. The dashed line in Fig. 2 shows the fitting result which seems to agree well with the data and is given by the equation $E_{g}(y) = 1.829 - 4.571 y$ eV. Based on the available data in Fig. 2 and the least-squares fits to the BAC model, the interaction potential of InGaPN alloys is obtained as $V = 1.449 \pm 0.170$ eV. From the BAC fitting results, the predicted $E_{g}$ transitions are 2.079 and 2.105 eV for $y=0.005$ and 0.010, respectively, and are indicated by the dotted arrows in Fig. 1. The $E_{g}$ subbands for both samples are close to the $E_{g}$ level and hence have a localizedlike character. Since the dipole interaction for optical transitions couples much more strongly to extended states than to the localized states, it is expected that the character of the conduction subband wave functions will affect the intensity of the optical transitions from the valence band to the $E_{g}$ subband. This could explain the failure to observe $E_{g}$ transitions in the PR spectra of the samples with $y=0.005$ and 0.010.

FIG. 2. Triangle and the squares, respectively, represent the energy positions of the $E_1$ and $E_2$ (or $E_0$ for $y=0$) transitions obtained from the PR spectra of In$_{\text{x}}$Ga$_{\text{1-x}}$P$_{0.995}$N$_{0.005}$ as a function of nitrogen composition. The solid lines are the least-squares fits to the BAC model. The dotted line marks the energy position of $E_1$ relative to the valence-band top. The open circles represent the band-gap energy $E_{g}$ of InGaP considering only the strain and ordering effects as discussed in the text. The dashed line is the linear fit to $E_{g}$.
with temperature does not slow down in our investigation. We employ a temperature dependent as well as a temperature independent $E_N$ level to describe the band-gap variation by Eq. (1). Assuming that $E_\Gamma(T)$ of sample A follows the temperature dependence of the band gap of In0.53Ga0.47As, and therefore shares the same Varshni coefficients as In0.53Ga0.47As, the values of $E_\Gamma(T)$ of sample A at various temperatures can be evaluated with $E_\Gamma(293)$ assigned as 1.813 eV which is obtained in our calculation above. The dotted line in Fig. 4 represents the $E_\Gamma(T)$ values for sample A evaluated from Eq. (1) with a constant $E_N$=2.040 eV, $V$ =1.240 eV, and the $E_\Gamma(T)$ calculated above. When the $E_\Gamma(T)$ level is assumed also to follow the band gap temperature dependence of InGaP, the results predicted by the BAC model are shown by the solid line. Apparently the assumption of a temperature-dependent $E_N$ level gives a better fit with the experimental data, as in the case of GaPN.\textsuperscript{3} The observation of temperature dependence of the $E_N$ level in InGaP contrast with those reported by Ref. 5 which justifies confirmatory investigation and detailed theoretical analysis of more InGaPN samples with different indium compositions.

In conclusion, not only the band gap ($E_\sigma$ or $E_\tau$, transition) but also the upper $E_\lambda$ transition of InGaPN grown on GaAs substrates are observed in PR spectra. The BAC model is introduced to describe the dependence of the energy positions of the two subbands on the N content. In addition to the contributions of the epitaxial-strain and atomic-ordering effects, the band-gap reduction in the InGaP alloys is also caused by the N incorporation. By assigning $E_N$=2.040 eV, the interaction potential $V$ is obtained as 1.449±0.170 eV at 293 K. In contrast to the published results in Ref. 5, the incorporation of a temperature-dependent $E_N$ level into the BAC model gives a better fit with the experimental data. These diverging interpretations of the temperature dependence of the $E_N$ level in InGaPN merit further investigation.

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