Studies of band alignment and two-dimensional electron gas in InGaPN/GaAs heterostructures

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Room-temperature photoreflectance (PR) and photoluminescence (PL) spectra are measured for a series of In0.54Ga0.46P1−xNy/GaAs heterostructures grown on GaAs (100) substrate. Redshifts of the PR and PL peaks indicate that the band gap of In0.54Ga0.46P1−xNy is dramatically reduced as nitrogen is incorporated. The emergence of additional peaks in PR spectra as nitrogen is incorporated indicates that the band alignment switches from type I to type II, due to the lowering of the conduction band, thus forming a two-dimensional electron gas (2DEG) in the interface region between In0.54Ga0.46P1−xNy and GaAs. The band gap energy and transition energies between the confined levels in the 2DEG are determined for samples with various nitrogen concentrations y. The number of confined levels in the 2DEG is found to increase with y; the composition-dependent bowing parameter is determined. © 2005 American Institute of Physics. [DOI: 10.1063/1.1855406]

Lattice-matched In0.49Ga0.51P grown on a GaAs substrate has recently attracted considerable attention; it has been widely used in optoelectronic and electronic devices, such as semiconductor lasers, heterojunction bipolar transistors, and high efficiency tandem solar cells. A small amount of nitrogen incorporation is known to reduce dramatically the band gap energy in InGaAs; the reduction results mostly from the lowering of the conduction band. The nitrogen incorporated into InGaP has recently been reported to have a similar effect. However, few relevant research reports have been published. Additionally, most studies have employed photoluminescence (PL) spectra at low temperature; therefore, most of the electro-optical properties examined have been limited to low temperature. Detailed studies of the electro-optical characteristics at room temperature and high temperature are interesting, necessary, and important.

This letter describes the feasibility of using room-temperature photoreflectance spectroscopy (PR) to elucidate the electro-optical properties of a series of In0.54Ga0.46P1−xNy/GaAs heterostructures. The PR spectra enable the band gap energy, band alignment, built-in electric field, and transition energies between the confined levels of the two-dimensional electron gas (2DEG) to be accurately determined at various contents of incorporated nitrogen. Room-temperature PL spectra are also measured in this study to verify some results from PR studies. Experimental results reveal that, as y ≥ 0.005, the band offset of the conduction band of In0.54Ga0.46P1−xNy falls dramatically so that the band alignment switches from type I to type II, and a 2DEG forms at the interface in the heterostructures. The band offset and thus the number of transition energies in 2DEG increases with the content of the incorporated nitrogen.

In0.54Ga0.46P1−xNy/GaAs heterostructures are grown on (1 0 0) GaAs semi-insulating substrate by gas source molecular beam epitaxy. The growth sequence entails a 0.5-μm-thick In0.54Ga0.46P1−xNy (y=0−2%) undoped layer grown on a 0.2 μm thickness of a GaAs buffer layer which is first grown on the GaAs substrate. The growth temperature at the substrate ranges between 340 and 480 °C with a nitrogen plasma ignited. No samples are thermal annealed. The mole fractions and lattice mismatch between In0.54Ga0.46P1−xNy and GaAs were determined by double-crystal x-ray diffractometry. All samples possess compressive strain on the GaAs buffer layer. The strain decreases as the nitrogen content increases. Table I lists the lattice mismatches of samples with various nitrogen concentrations.

PL was measured at room temperature with the 532 nm line of a solid-state laser as the excitation source. A Si photodetector was used to detect the signal through a lock-in amplifier at the exit of a quarter meter monochromator. The standard arrangement of the PR apparatus was used. He–Cd or He–Ne laser served as the pumping beam. The detection system comprises a Si photodetector and a lock-in amplifier.

Figure 1(a) depicts the room-temperature PL spectra of three In0.54Ga0.46P1−xNy samples with y=0, 0.005, and 0.010, respectively. No PL signal is observed in the sample with y=0.020. As the nitrogen concentration increases, the PL intensity decreases rapidly. Additionally, the peak position shows a redshift, apparently indicating that the band gap energy of In0.54Ga0.46P1−xNy reduces markedly; and the full width at half maximum (FWHM) of the peak broadens considerably as well. The band gap energies which correspond to the peak positions are 1.832, 1.786, and 1.750 eV for samples with y=0, 0.005, and 0.010, respectively.

Hong et al. have found no GaAs QW PL emission from In0.54Ga0.46P1−xNy/GaAs/In0.54Ga0.46P1−xNy multiple quantum well when y is equal to or larger than 0.012. Two possibilities are suggested. One is that high nitrogen composition lowers the level of the conduction band so much that the energy band alignment switches from type I to type II when...
the nitrogen composition is higher than 1.2%; the other possibility is that higher nitrogen composition creates more nonradiative centers, thus reducing the PL intensity. As nitrogen concentration $y$ is higher than 0.012, the density of the nonradiative centers becomes sufficiently large to suppress all PL emission. They, however, are unable to determine which mechanism is dominant. To discern which mechanism is responsible for the absence of PL emission, we measure the PR mechanism is dominant. To discern which mechanism is responsible for the absence of PL emission, we measure the PR spectra of a series of In$_{0.54}$Ga$_{0.46}$P$_{1-y}$N$_y$ samples with $y=0, 0.005, 0.010, 0.020$, respectively. These results are also included in Table I.

The reduction of band gap energy in In$_{0.54}$Ga$_{0.46}$P with the incorporation of a small amount of nitrogen can be described by

$$E_g(\text{In}_{0.54}\text{Ga}_{0.46}\text{P}_{1-y}N_y) = yE_g(\text{In}_{0.54}\text{Ga}_{0.46}N) + (1 - y)E_g(\text{In}_{0.54}\text{Ga}_{0.46}P) + by(1 - 1),$$

where $b$ is the bowing coefficient. The bowing coefficient is found to be of the same order as for the incorporation of nitrogen in InP ($b=16$ eV) and GaP ($b=14$ eV). For GaAs and InGaAs, $b$ ranges from 10 to 20 eV, depending on compositions. The bowing coefficients of In$_{0.54}$Ga$_{0.46}$P$_{1-y}$N$_y$ depend on nitrogen composition and are 11.15, 9.07, and 10.72 eV for $y=0.005, 0.010, 0.020$, respectively. These results are also included in Table I.

Figure 2 displays room-temperature PR spectra from 1.25 to 1.60 eV. Additional features (indicated by arrows) appear in the PR spectra at energies lower than the band gap energy.

<table>
<thead>
<tr>
<th>$y$</th>
<th>Mismatch $(\Delta d/d)$ $\times 10^{-3}$</th>
<th>Bowing parameter $b(y)$ (eV)</th>
<th>$E_g$ of InGaPN (eV)</th>
<th>$E_g$ of GaAs (eV)</th>
<th>Energy levels of 2DEG (eV)</th>
<th>Electric field at the interface (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.20</td>
<td>$\cdots$</td>
<td>1.843</td>
<td>1.427</td>
<td>$\cdots$</td>
<td>25.9</td>
</tr>
<tr>
<td>0.005</td>
<td>8.09</td>
<td>11.15</td>
<td>1.786</td>
<td>1.393</td>
<td>$\cdots$</td>
<td>17.8</td>
</tr>
<tr>
<td>0.010</td>
<td>7.12</td>
<td>9.07</td>
<td>1.751</td>
<td>1.369</td>
<td>$\cdots$</td>
<td>16.2</td>
</tr>
<tr>
<td>0.020</td>
<td>6.45</td>
<td>10.72</td>
<td>1.628</td>
<td>$\cdots$</td>
<td>1.345</td>
<td>14.1</td>
</tr>
</tbody>
</table>
energy of GaAs for nitrogen composition \( y \neq 0 \). Although some of these features are relatively weak due to inconsistency of the sample quality, these features can be attributed to the transitions between the confined levels in the 2DEG at the interface between GaAs and In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_{y}\). As is well known, in the sample In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_{y}\)/GaAs where nitrogen concentration \( y = 0 \), the band alignment is type I, as shown in Fig. 3(a). No 2DEG exists in the conduction band and the only feature at 1.42 eV in the PR spectrum corresponds to the GaAs band gap transition. The incorporation of nitrogen dramatically reduces the band gap energy in In\(_{0.54}\)Ga\(_{0.46}\)P; most of the reduction results from lowering the conduction band. As \( y \geq 0.005 \), the band alignment switches from type I to type II; a triangular potential well is formed in the conduction band at the interface of heterostructures, as shown in Fig. 3(b); 2DEG is formed in the conduction band. The larger nitrogen concentration implies a deeper triangular potential well and more confined levels in the 2DEG. Only one 2DEG transition is observed in the sample with \( y = 0.005 \), while two and four 2DEG transitions are observed in samples with \( y = 0.010 \) and \( 0.020 \), respectively. All 2DEG transition peaks were well fitted to Eq. (1) using the first derivative of a Lorentzian function, where \( m_j = 2 \) corresponds to an excitonic transition. The energies corresponding to each 2DEG transition are indicated by the arrows in Fig. 2 and to an excitonic transition. The energies corresponding to each 2DEG transition are indicated by the arrows in Fig. 2 and to an excitonic transition. The energies corresponding to each 2DEG transition are indicated by the arrows in Fig. 2 and to an excitonic transition. The energies corresponding to each 2DEG transition are indicated by the arrows in Fig. 2 and to an excitonic transition. The energies corresponding to each 2DEG transition are indicated by the arrows in Fig. 2 and to an excitonic transition.

The very weak PL signal observed in the sample with \( y = 0.005 \) may be due to the fact that the band offset is extremely small (\( \approx 6 \) meV) such that the band alignment lies between type I and type II.

In Fig. 2, the features above 1.42 eV are the Franz–Keldysh oscillations (FKOs) associated with the electric field at the interface between the GaAs buffer layer and In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_{y}\). The GaAs band gap transitions in the PR spectra of some samples are not very pronounced because of inconsistency in the sample quality and the coupling among different features of the PR spectra. The band gap energy and the built-in electric field \( F \) can be accurately obtained from the FKOs. The extreme of FKO occurs when

\[
E_n = \hbar \Omega F_n + E_g, \quad n = 0, 1, 2, 3, \ldots
\]

with \( F_n = [3\pi(n+1/2)/2]^{2/3} \), where \( n \) and \( E_g \) are the index and photon energy of the \( n \)th extreme, respectively. \( \hbar \Omega \) is the electro-optic parameter, given by \( (\hbar \Omega)^3 = e^2\hbar^2 F^2/8\mu \), where \( \mu \) is the reduced interband effective mass of the electron and heavy hole pair in GaAs in the direction of the electric field \( F \). The FKO extreme \( E_n \) plotted against \( F_n \) yields a straight line with a slope of \( \hbar \Omega \) and an intercept \( E_g \). Thus, \( F_n \) and \( E_n \) can be deduced from such plot. Table I lists the band gap energies of GaAs, the electric fields \( F \) at the interface, and lattice mismatches for all samples with various nitrogen contents. The electric field declines rapidly from 25.9 kV/cm as soon as the nitrogen is incorporated and then declines linearly from 17.8 to 14.1 kV/cm, as the nitrogen content is raised from 0.5% to 2.0%. In contrast, as \( y \) increases from 0 to 0.005, the lattice mismatch decreases gradually; and as \( y \) increases from 0.005 to 0.020, the lattice mismatch declines rapidly and linearly. Accordingly, the electric field is more strongly correlated with the concentration of nitrogen than with the lattice mismatch.

In summary, room-temperature PR spectra have been proven to be useful in determining the band gap and the transition energies associated with the energy levels in 2DEG at various nitrogen concentrations. These are unobservable in the PL spectrum. Nitrogen incorporation dramatically reduces the energy band gap of In\(_{0.54}\)Ga\(_{0.46}\)P. The concentration-dependent bowing parameters are determined. When the content of incorporated nitrogen is \( y = 0.005 \), the band alignment In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_{y}\)/GaAs is found to switch from type I to type II, due to the lowering of the conduction band. The absence of GaAs QW PL emission in the In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_{y}\)/GaAs/In\(_{0.54}\)Ga\(_{0.46}\)P\(_{1-y}\)N\(_{y}\) multiple QW as \( y = 0.012 \) observed by Hong et al. is shown to be due to type II band alignment.

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