Effects of weak ordering of InGaPN

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The effect of weak ordering on InGaPN/GaAs heterostructure grown by gas source molecular-beam epitaxy is quantitatively studied by room-temperature Raman, photoluminescence (PL), and photoreflectance spectroscopy in this work. The PL intensity decreases rapidly as the nitrogen concentration increases, implying that more nonradiative centers are generated by the ordering effect and the degradation of the samples. The band gap of InGaPN decreases dramatically as the nitrogen is incorporated. The Raman modes of InGaPN between 130 and 1000 cm −1 are analyzed. Polarized Raman spectra reveal that the InGaPN layers become more ordered as more nitrogen is incorporated. A broad Raman structure that appeared around 730 cm −1 is attributed to an InGaN-like LO-phonon mode. The transition of the crystal structure from the zinc blende to CuPt structure and the formation of GaN clusters are responsible for the ordering effect in the InGaPN layer. © 2005 American Institute of Physics. [DOI: 10.1063/1.1940118]

Recently, the In0.54Ga0.46P1−yNy/GaAs heterostructures grown by gas source molecular beam epitaxy (GSMBE) have been intensively investigated. Incorporation of a small amount of nitrogen in InGaP has been reported to substantially reduce the band gap energy; most of the reduction is caused by lowering of the conduction band.1 Accordingly, InGaPN is a suitable material for use as the emitter and collector of blocked-hole bipolar transistors.1 An interesting characteristic of InGaP is the ordering effect that is governed by growth parameters, such as growth rate, III-V ratio, substrate temperature, and substrate misorientation.2–4 The ordering is caused by the transition from the disordered zinc blende structure to an ordered CuPt structure. This effect reduces the band gap, splits the valence band,5 and affects the optical and electronic properties of the materials. Besides, Hashimoto et al.6 have reported that incorporating guest atoms may induce long-range order. Accordingly, incorporating various amounts of nitrogen could induce various degrees of ordering in InGaP.

This work reports the observation of a weak ordering effect of In0.54Ga0.46P1−yNy/GaAs heterostructures, as elucidated by Raman spectra, which is a quantitative and nondestructive method for studying the crystal structures and the electronic and phonon characteristics of the materials. Photoluminescence (PL) and photoreflectance (PR) spectra are also obtained to verify the optical characteristics deduced from the Raman spectra. In0.54Ga0.46P1−yNy/GaAs heterostructures are grown on a (1 0 0) GaAs semi-insulating substrate by gas source molecular beam epitaxy (GSMBE). The growth sequence involves the growth of a 0.5-μm-thick undoped In0.54Ga0.46P1−Ny (y = 0, 0.005, 0.010, and 0.020) layer on a 0.2-μm-thick GaAs buffer layer. The growth temperature is maintained at approximately 420 °C, with nitrogen plasma ignited. The samples are not thermally annealed after growth. The mole fraction and lattice mismatch between In0.54Ga0.46P1−Ny and GaAs are determined by double-crystal x-ray diffractionometry. All samples exhibit a compressive strain on the GaAs buffer layer. The strain decreases as the nitrogen content increases. Table I presents the lattice mismatch of all samples with various nitrogen concentrations.

Raman, PL, and PR spectra are measured at room temperature. For the details of PL and PR measurements, please refer to our previous report.1 For Raman spectrum measurement, the laser beam of 532 nm wavelength, serving as the excitation light source, is focused using a ×100 microscopic objective, and the power on the sample is maintained at 10 mW. The scattered light is also collected by the objective and analyzed with a J. Y. Ramanor U 1000 double monochromator, equipped with a cooled charge coupled device detector. The resolution of the Raman system is 0.2 cm −1. All measurements are performed with a backscattering geometry on the (1 0 0) face of the samples; the propagation directions of the incident laser and scattered light are Z′ = [001] and Z′′ = [001], respectively. Various polarization directions of the incident laser beam and scattered light are specified as X′ = [110], Y′ = [110], X′′ = [100], and Y′′ = [010], respectively.2

The room-temperature PL and PR spectra of four In0.54Ga0.46P1−yNy samples with y = 0, 0.005, 0.010, and 0.020 can be found in our previous letter.1 As the nitrogen concentration increases, the PL intensity decreases rapidly, suggesting that more and more nonradiative centers are generated.

Table I. The sample composition, lattice mismatch, normalized PL intensity, frequency shift of Ga-like LO mode, and c ratio in In0.54Ga0.46P1−yNy/GaAs samples.

<table>
<thead>
<tr>
<th>y</th>
<th>Mismatch (Δd/d)10−3</th>
<th>Normalized PL intensity</th>
<th>Freq. of GaP-like LO mode (cm−1)</th>
<th>c ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.20</td>
<td>1.00</td>
<td>379.4</td>
<td>4.77</td>
</tr>
<tr>
<td>0.005</td>
<td>8.09</td>
<td>0.05</td>
<td>377.9</td>
<td>2.03</td>
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<tr>
<td>0.010</td>
<td>7.12</td>
<td>0.12</td>
<td>377.5</td>
<td>1.59</td>
</tr>
<tr>
<td>0.020</td>
<td>6.45</td>
<td>...</td>
<td>376.8</td>
<td>1.17</td>
</tr>
</tbody>
</table>

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It has been reported that ordered samples have more nonradiative loss mechanisms than disordered samples. The increase in nonradiative centers can be attributed to the increase in the degree of ordering and defects as the nitrogen concentration is increased. The band gap energies that correspond to the peak positions are 1.832, 1.786, and 1.750 eV for samples with nitrogen concentrations of 0, 0.005, and 0.010, respectively. The band gap energy of In_{0.54}Ga_{0.46}P_{0.98}N_{0.02} determined from photoreflectance spectrum is 1.628 eV. As the nitrogen concentration y is increased from 0 to 0.020, the band gap energy, which is affected by nitrogen composition and the ordering effect, is reduced by 204 meV. Raman spectra are measured from 130 to 1000 cm\(^{-1}\) to determine whether ordering contributes to the band gap reduction. No Raman mode is observed from the GaAs buffer layer because the InGaPN layer on top is too thick to allow the incident light to penetrate to the GaAs buffer layer. For clarity, the Raman modes are analyzed at low, medium, and high frequencies.

Figure 1(a) depicts the Raman spectra taken in samples with Z(\(Y', Y'\))\(\overline{Z}\) scattering geometry in the low frequency range from 130 to 250 cm\(^{-1}\). The broad structure observed around 200 cm\(^{-1}\) consists of two features, one of which is the disorder-activated longitudinal acoustic (FLA) phonon mode (~208 cm\(^{-1}\)). According to Raman selection rules, the intensity of the FLA mode increases with increasing ordering of the sample. Therefore, the slight increase of the intensity of the FLA peak in Fig. 1(a) with nitrogen concentration implies that the degree of ordering of the sample indeed increases with nitrogen concentration.

Figure 1(b) shows the Raman spectra of all samples in the medium frequency range taken in the Z(\(X', X'\))\(\overline{Z}\) scattering configuration. Because the nitrogen concentration is dilute, the typical Raman modes of InGaP are still observable in the spectra. The peaks at 380 and 360 cm\(^{-1}\) are the GaP-like longitudinal optical (LO) phonon mode and the InP-like LO-phonon mode, respectively, while the broad peak around 325 cm\(^{-1}\) is the InP-like transverse optical (TO)-phonon mode. In addition, there is another weak mode at about 371 cm\(^{-1}\) which is called GaP-like TO-phonon mode coupled with the modes at 360 and 380 cm\(^{-1}\). Although the TO modes are forbidden in the zinc-blende structure by the selection rules in the ideal back scattering configuration, the appearance of TO modes may result from a small deviation from back scattering. Notably both the Raman intensities of the InP-like LO and GaP-like LO modes increase slightly with an increase of nitrogen concentration. The intensities as a function of the nitrogen composition are plotted in Fig. 2. The b/a ratios, where a and b are shown in Fig. 1(b), are also plotted in Fig. 2. A decrease in the valley-to-peak intensity ratio (b/a) with an increasing nitrogen content is observed. The trends of the intensities of the InP-like LO and GaP-like LO modes and the b/a ratio with nitrogen content are consistent with the observation by Yoon et al. for InGaP.

This result infers that In_{0.54}Ga_{0.46}P_{1−y}N\(_{y}\) becomes more ordered as more nitrogen is incorporated. The relatively large b/a ratio ranges from 0.335 to 0.408, indicating that the degree of ordering is relatively small in our samples as compared with those observed in Ref. 2, in which the InGaP samples studied were grown by metalorganic vapor phase epitaxy (MOVPE) and were more ordered. In addition, redshift is observed on the GaP-like LO phonon with increasing nitrogen content. This is attributed to the superposition of GaP-like LO phonon with the increasingly active GaP-like TO phonon at about 371 cm\(^{-1}\) in more ordered material. The frequency shifts are listed in Table I. The gradual decline in b/a ratio may be also due to the growth of GaP-like TO mode.

It is well known that the degree of ordering of InGaP is due to the difference in atomic structures. In disordered phase, the crystal symmetry is a cubic zinc blende structure with point group \(T_\text{d}\), and in ordered phase, it is trigonal structure with point group \(C_{3v}\). From the Raman selection rules, the first-order LO-phonon scattering is forbidden in \(T_\text{d}\) crystal group symmetry with the configuration of parallel polarization (\(X', X'\)), but is allowed in crossed polarization geometry (\(X''', Y''\)).

The polarized Raman spectra of In_{0.54}Ga_{0.46}P_{1−y}N\(_{y}\) with various nitrogen concentrations are measured for two scattering geometries Z(\(X', X'\))\(\overline{Z}\) and Z(\(X'', Y''\))\(\overline{Z}\). Only the spectra of the samples with \(y=0\) and 0.020 are shown in Fig. 3. Table I also lists the parameter c defined as the ratio of intensities of GaP-like LO phonon in (\(X'', Y''\)) to (\(X', X''\)) polarization geometries. The decrease of parameter c suggests that the InGaPN crystal structure deviates more from the disordered \(T_\text{d}\) symmetry and is closer to the ordered \(C_{3v}\) symmetry. This again demonstrates that InGaPN is more ordered with increasing nitrogen concentration.

The observation of increasing ordering effect from Raman spectra is consistent with the result of PL spectra mentioned above. However, in the most ordered sample (\(y = 0.020\)), the sharp Raman signal at 354 cm\(^{-1}\) reported in
The ordering effect in InGaPN samples can be attributed to the formation of different atomic structures and GaN clusters.6,11 The ordering effect in InGaPN samples can be attributed to GaN clusters.6,11 Moreover, the GaN bonds or clusters make a larger contribution to the InGaPN-like LO mode than InN bonds. In addition to the variation of atomic structure (zinc blende to CuPt structure), the GaN clusters also create the ordering effect in InGaPN samples. These conclusions completely agree with the report that the formation of spontaneous ordering in GaAsN may be related to the formation of GaN clusters.6,11

In conclusion, the In0.54Ga0.46P1−xN samples with nitrogen incorporated. However, the relatively large "b/a ratio and the absence of the peak at 354 cm−1 indicate that the degree of ordering in the GSBME-grown InGaPN samples is relatively weak in comparison with MOVPE-grown InGaP samples. The broad Raman structure that appears around 730 cm−1 is attributed to the InGaPN-like LO-phonon mode. The ordering effect in InGaPN samples can be attributed to the formation of different atomic structures and GaN clusters.

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FIG. 3. Raman spectra of In0.55Ga0.45P1−xN y samples with both the parallel polarization configuration (X′,Y′) and the crossed polarization configuration (X″,Y″).

FIG. 4. Nonpolarized Raman spectra of In0.55Ga0.45P1−xN y samples in the high frequency region. The broad InGaN-like LO mode is observed for all samples with y ≠ 0.