Mismatch strain as a driving force for the annealing-induced formation of In–N bonds in (In,Ga)(As,N)

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The mismatch strain and local bonding of N atoms in epitaxial (In,Ga)(As,N) layers has been studied by Raman spectroscopy in connection with cluster-Bethe-lattice calculations. The frequency of GaAs-like phonons is found to be applicable for a characterization of the average strain in the epilayers by using a consistent approximation for the composition dependencies. The analysis of N-related vibrational modes reveals that the preferential formation of In-N bonds during thermal annealing is driven not only by the local strain distribution, but correlates also with the average mismatch strain in (In,Ga)(As,N) via strain inhomogeneities on a longer length scale. © 2005 American Institute of Physics. [DOI: 10.1063/1.2043251]

Dilute group-III arsenide–nitrides have gained considerable attention because of their potential for GaAs-based optoelectronic devices in the technologically important wavelength range between 1.3 and 1.55 μm. 1 The unique properties of dilute group-III arsenide–nitrides are based on the incorporation of an element such as N with highly dissimilar properties compared to the host lattice atoms. The incorporation of In into Ga(As,N) strongly affects the local bonding of the N atoms by changing the local strain distribution as well as the formation of In-N bonds with an abundance beyond the expectation for a random alloy. 2,3

Recently, the correlated spatial redistribution of In and N in a (In,Ga)(As,N) quantum well structure upon thermal annealing was studied by transmission electron microscopy. 4 The driving force for the diffusion behavior has been explained by the reduction of the local strain, which is due to the observed increase in the probability to create an In-rich environment for N atoms. The influence of strain inhomogeneities on a longer length scale should be connected with the absolute level of the average strain which determines the size of the strain gradients. Thermally activated atomic diffusion depends on such gradients in composition and/or strain. Indeed, for (In,Ga)As/GaAs epitaxial layers, a clear correlation between average strain and atomic diffusion has been found. 5 Changes in the local environment of N atoms in (In,Ga)(As,N) can be observed by vibrational-mode spectroscopy. 2,3,6–8 We have studied the influence of the average mismatch strain on the annealing-induced modifications in the N-bond formation in (In,Ga)(As,N) layers by Raman spectroscopy. The assignment of the vibrational modes is accomplished by a cluster-Bethe-lattice simulation. 9

All investigated samples were grown by solid-source molecular beam epitaxy on GaAs(001) substrates using rf plasma sources for nitrogen supply. Details of the growth conditions have been published elsewhere. 10 The nominal N content in the (In,Ga)(As,N) layers was varied between 0.5% and 3.8% and the In content between 10% and 30%. An important requirement for comparison is that the conditions of two-dimensional growth were preserved. The thickness (200 nm) of the layers, which were capped by a GaAs layer of 5 nm thickness, has been chosen according to this requirement. Rapid thermal annealing was performed at a temperature of 800 °C for 60 s by using a Jetfirst 100 furnace. In order to avoid arsenic desorption, the samples were proximity capped with a GaAs wafer during the annealing process. The Raman measurements were carried out in the backscattering configuration from the epilayer surfaces with the samples cooled to a temperature of 20 K in a continuous-flow cryostat. The scattered light was analyzed by a single-path spectrograph equipped with a cooled charge-coupled-device array. For optical excitation, we used a He–Ne laser with a photon energy of 1.96 eV.

The strain in the (In,Ga)(As,N) layers has been examined by utilizing the measured frequencies of the GaAs-like LO-phonon lines (LO1) in the Raman spectra. Here, the difficulty lies in the fact that the phonon frequencies, which are well-known for the binary components, depend not only on the average strain in the (In,Ga)(As,N) layers but also on the composition, i.e., the In and N contents x and y. The strain-induced shift of the LO1-phonon frequency ∆ωM(x,y) can be expressed as ωM(x,y)=ωM(0)+α(x,y)δx(y), where ωM is the measured LO1-phonon frequency in the (In,Ga)(As,N) layers, ωM(x,y) the frequency for the unstrained alloy, and δx(y) the average strain. The frequency for the unstrained alloy has been approximated by ωM(0)=(295–42x–40y)cm−1. Here, the In-induced shift is assumed to lie between the values given in Refs. 11,12; the N-induced shift has been chosen in accordance with Refs. 13,14. The resulting strain-induced shift of the LO1-phonon line is shown in Fig. 1 as a function of the maximum possible average strain ϵmax, given by the lattice constants of coherently strained epilayers according to Vegard’s law. The negative value obtained for nearly lattice-matched layers (ϵmax ≈ 0) is presumably caused by the uncertainty in the N-induced shift of ωN. The slope α=480 cm−1 of the solid line in Fig. 1 is in agreement with, e.g., Ref. 14 and well describes the strain-induced phonon shift for ϵmax < 1.3%. That means, our approximation for the composition dependence is consistent with the assumption of coherent strain in these layers. The LO1-phonon frequency of the sample with the largest nominal mismatch strain deviates strongly from this behavior, which provides evidence for strain relaxation. These Raman results were confirmed by x-ray diffraction measurements revealing coherent strain in

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the layers with \( \epsilon_{\text{max}} < 1.3\% \) and complete strain relaxation in the sample with \( \epsilon_{\text{max}} = 2.05\% \). For the discussion below, it is important to note that the obtained average strain is not a monotonous function of the In or N content in the epilayers (cf. Table I). In the following, we assume the actual average strain \( \epsilon \) for the investigated layers (cf. Table I).

Raman spectra of (In,Ga)(As,N) samples with an In content of [In]=11% and a N content of [N]=3.8% as well as with [In]=20% and [N]=1.5% are shown in Fig. 2. The chemical compositions of the (In,Ga)(As,N) layers correspond to mismatch strain values of \( \epsilon = 0.03\% \) [cf. Figs. 2(a) and 2(b)] and 1.13% [cf. Fig. 2(c)]. For the layer with \( \epsilon = 0.03\% \), spectra are shown for samples before [cf. Fig. 2(a)] and after [cf. Fig. 2(b)] thermal annealing. The Raman features at frequencies larger than 500 \( \text{cm}^{-1} \) are due to second-order scattering by GaAs-like optical (TO\(_1\) and LO\(_1\)) phonons, whereas N-related vibrational modes are observed in the frequency range between 450 and 500 \( \text{cm}^{-1} \). This part of the spectra can be regarded as a superposition of three modes labeled as \( A_1, T_2, \) and \( E \). For an assignment of the Raman peaks, we performed cluster-Bethe-lattice calculations\(^9\) of N-related vibrational modes in (In,Ga)(As,N). The resulting densities of states for different bonding configurations are shown in Fig. 3 with all peaks labeled by the respective mode symmetries. The Ga–N force constants \( f_{\text{Ga–N}} \) have been chosen in accordance with Alt et al.\(^6\) The increase in the Ga–N force constant can be explained by the shortening of the Ga–N bonds induced by the incorporation of In, i.e., the larger size of the In atom and the lower strength of the In–N bond result in an increase of the Ga–N bond-stretching force constant. The calculated vibrational spectra can be regarded as fingerprints for the different bonding configurations. The Raman peak labeled as \( T_2 \) is attributed to Ga\(_3\)N, i.e., to N with four Ga atoms as nearest neighbors [cf. Fig. 3], whereas the modes \( A_1 \) and \( E \) belong to the configuration Ga\(_3\)In\(_2\)N with one In–N bond and three Ga–N bonds [cf. Fig. 3]. The contribution of the configuration Ga\(_3\)In\(_2\)N [cf. Fig. 3] is assumed to be small. The Raman feature at 530 \( \text{cm}^{-1} \) observed for the sample with \( \epsilon = 1.13\% \) [cf. Fig. 2(c)] is too broad and too high in frequency to be associated with the mode \( B_1 \) of the configuration Ga\(_3\)In\(_2\)N. It should be noted that our assignments agree with those in Ref. 6, but differ somewhat from the ones given in Ref. 7.

Thermal annealing leads to a considerable increase of the contribution from Raman scattering by the Ga\(_3\)In\(_2\)N configuration, which becomes apparent from a comparison of the spectra in Figs. 2(a) and 2(b) of the nearly lattice-matched (\( \epsilon = 0.03\% \)) sample. Note that the probability to find one In as a nearest neighbor of N is equal to the In content, which has a maximum value of 30\% in the investigated samples. In accordance with the work of Alt et al.\(^6\) the probability for the In–N bond formation seems to be clearly larger than expected for a random alloy situation in all samples (before and after annealing). As a measure for the abundance of In–N bonds, we determined the ratio \( r \) between the integrated Raman intensity of modes \( A_1 \) and \( E \) (Ga\(_3\)In\(_2\)N) and the one of mode \( T_2 \) (Ga\(_3\)N) given by \( r = a_{A_1}/a_{E} = (I_{A_1} + I_{E})/I_{T_2} \) for a series of samples, as-grown (\( r_{\text{ag}} \)) as well as after annealing (\( r_{\text{an}} \)). The relative change of the In–N bond abundance due to thermal annealing (\( r_{\text{an}}/r_{\text{ag}} \)) is shown in Fig. 4 as a function of the nominal mismatch strain. Note that the layer with a nominal mismatch strain of 2.05\% is com-

![FIG. 1. Strain-induced shift of the LO\(_1\)-phonon line obtained from Raman spectra of the investigated (In,Ga)(As,N) layers given by \( \Delta \omega_{\text{LO}}(x,y) = \omega_{\text{max}} - \omega_{\text{LO}}(x,y) = 0.13\% \).

![FIG. 2. Raman spectra of (In,Ga)(As,N) layers with [In]=11\% and [N]=3.8\% (a) before and (b) after thermal annealing as well as (c) the spectrum of an annealed layer with [In]=20\% and [N]=1.5\%. The mismatch strain values \( \epsilon \) are indicated.](image)

| TABLE I. In content \( x(\%) \), N content \( y(\%) \), and average strain \( \epsilon(\%) \) of the investigated (In,Ga)(As,N) layers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = [\text{In}] )</td>
<td>11</td>
<td>12</td>
<td>20</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>( y = [\text{N}] )</td>
<td>3.8</td>
<td>0.5</td>
<td>1.5</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>0.03</td>
<td>0.76</td>
<td>1.13</td>
<td>1.23</td>
<td>0</td>
</tr>
</tbody>
</table>
pletely relaxed. The results clearly demonstrate a correlation between the average strain in the epilayers and the annealing-induced formation of In–N bonds. This means, besides the local strain, the average strain is also a driving force for the correlated redistribution of In and N atoms induced by thermal annealing via strain gradients created by inhomogeneities on a larger length scale. Consequently, the undesirable annealing-induced modifications in the properties of In,GaAs,N layers can be suppressed by choosing nearly lattice-matched alloy compositions.

In conclusion, we demonstrated that Raman spectroscopy in connection with cluster-Bethe-lattice calculations is a powerful tool to study the average mismatch strain as well as the local environment and redistribution of N atoms in epitaxial (In,Ga)(As,N) layers. For the strain analysis, a consistent approximation for the composition dependent GaAs-like LO-phonon frequency has been utilized. Most importantly, the average mismatch strain is found to be a driving force for preferential formation of In–N bonds during thermal annealing.

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