

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 dependences. 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 back-scattering 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 (LO_1) 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 LO_1 -phonon frequency $\Delta\omega_S(x,y)$ can be expressed as $\omega_M - \omega_A(x,y) = \alpha\epsilon(x,y)$, where ω_M is the measured LO_1 -phonon frequency in the (In,Ga)(As,N) layers, $\omega_A(x,y)$ the frequency for the unstrained alloy, and $\epsilon(x,y)$ the average strain. The frequency for the unstrained alloy has been approximated by $\omega_A(x,y) = (295 - 42x - 40y)\text{cm}^{-1}$. 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 LO_1 -phonon line is shown in Fig. 1 as a function of the maximum possible average strain ϵ_{max} , given by the lattice constants of coherently strained epilayers according to Vegard's law. The negative value obtained for nearly lattice-matched layers ($\epsilon_{\text{max}} \approx 0$) is presumably caused by the uncertainty in the N-induced shift of ω_A . The slope $\alpha = 480\text{cm}^{-1}$ of the solid line in Fig. 1 is in agreement with, e.g., Ref. 14 and well describes the strain-induced phonon shift for $\epsilon_{\text{max}} < 1.3\%$. That means, our approximation for the composition dependence is consistent with the assumption of coherent strain in these layers. The LO_1 -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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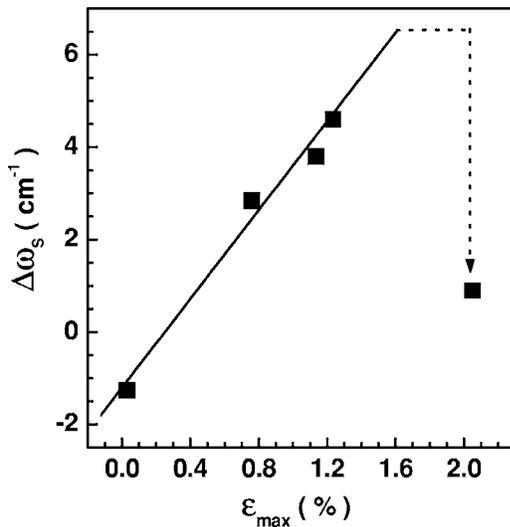


FIG. 1. Strain-induced shift of the LO₁-phonon line obtained from Raman spectra of the investigated (In,Ga)(As,N) layers given by $\Delta\omega_s(x,y) = \omega_M - \omega_A(x,y) = \alpha\epsilon(x,y)$.

the layers with $\epsilon_{\max} < 1.3\%$ and complete strain relaxation in the sample with $\epsilon_{\max} = 2.05\%$. 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 nominal values for the actual average strain ϵ in the nonrelaxed 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 cm⁻¹ are due to second-order scattering by GaAs-like optical (TO₁ and LO₁) phonons, whereas N-related vibrational modes are observed in the frequency range between 450 and 500 cm⁻¹. This part of the spectra can be regarded as a superposition of three modes labeled as A₁, T₂, and E. For an assignment of the Raman peaks, we performed cluster-Bethe-lattice calculations⁷ 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 T₂ is attributed to Ga₄N, i.e., to N with four Ga atoms as nearest neighbors [cf. Fig. 3], whereas the modes A₁ and E belong to the configuration Ga₃InN with one In–N bond and three Ga–N bonds [cf. Fig. 3]. The contribution of the configuration Ga₂In₂N [cf. Fig. 3] is assumed to be small. The Raman feature at 530 cm⁻¹ observed for the sample with $\epsilon = 1.13\%$ [cf. Fig. 2(c)] is too broad and too high in frequency to be

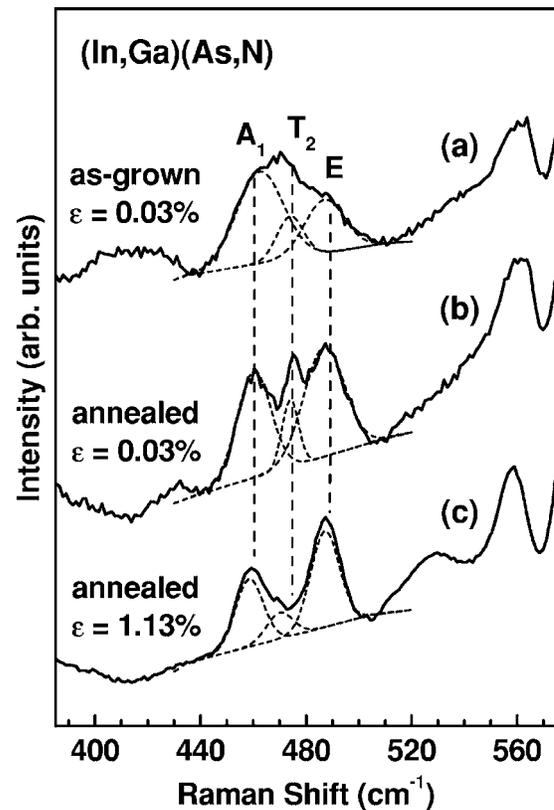


FIG. 2. Raman spectra of (In,Ga)(As,N) layers with [In]=11% and [N]=3.8% (a) before and (b) after thermal annealing as well as (c) the spectrum of an annealed layer with [In]=20% and [N]=1.5%. The mismatch strain values ϵ are indicated.

associated with the mode B₁ of the configuration Ga₂In₂N. 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 Ga₃InN 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 A₁ and E (Ga₃InN) and the one of mode T₂ (Ga₄N) given by $r = a_{3-1}/a_{4-0} = (I_{A1} + I_E)/I_{T2}$ for a series of samples, as-grown (r_{ag}) as well as after annealing (r_{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-

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

Sample	1	2	3	4	5
$x=[\text{In}]$	11	12	20	20	30
$y=[\text{N}]$	3.8	0.5	1.5	1.0	0.5
ϵ	0.03	0.76	1.13	1.23	0

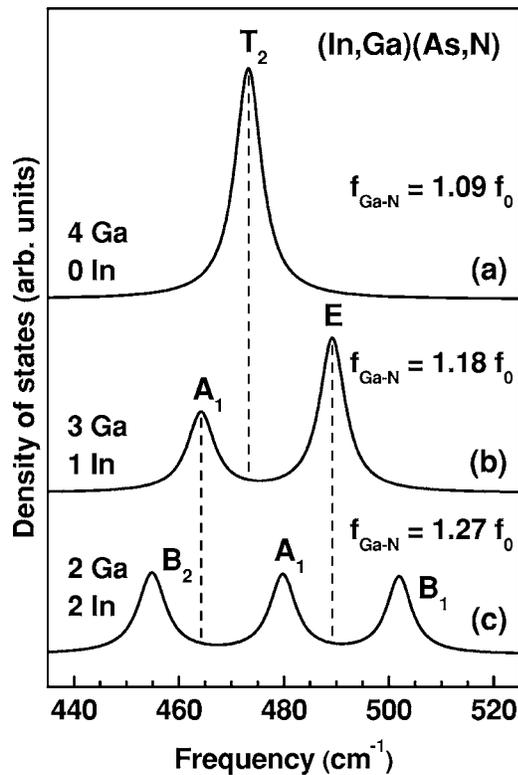


FIG. 3. Density of states for N-related vibrational modes in (In,Ga)(As,N) with different configurations of nearest neighbors as indicated. The chosen Ga–N force constants $f_{\text{Ga-N}}$ are given in terms of the Ga–As force constant f_0 .

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,Ga)(As,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

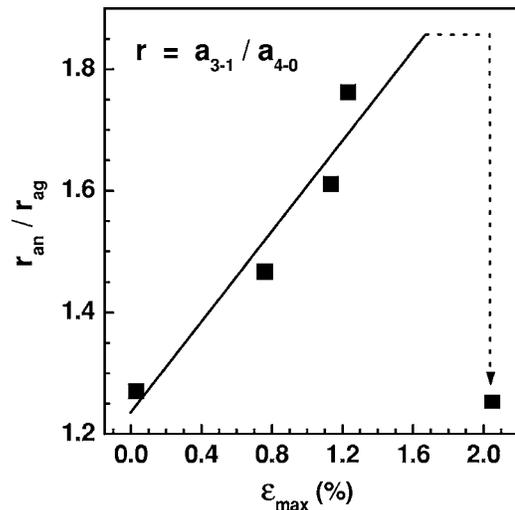


FIG. 4. Annealing-induced change in the abundance of In–N bonds $r_{\text{an}}/r_{\text{ag}}$ as a function of nominal mismatch strain, where $r_{\text{ag}}(r_{\text{an}})$ is the Raman intensity of N with one In atom as nearest neighbor (a_{3-1}) normalized to the one of N with four Ga neighbors (a_{4-0}) before (after) annealing.

force for preferential formation of In–N bonds during thermal annealing.

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