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Effect of annealing on the In and N distribution in InGaAsN quantum wells

M. Albrecht,[a] V. Grillo, T. Remmele, and H. P. Strunk
University of Erlangen-Nuremberg, Department of Materials Science and Engineering, Institute of Microcharacterisation, Cauerstr. 6, 91058 Erlangen, Germany

A. Yu. Egorov, Gh. Dumitras, and H. Riechert
Infineon Technologies, Corporate Research Photonics, Otto-Hahn-Ring 6, 81730 München, Germany

A. Kaschner, R. Heitz, and A. Hoffmann
Institute of Solid State Physics, Technical University of Berlin, Hardenbergstraße 36, 10632 Berlin, Germany

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We analyze the influence of annealing on compositional fluctuations in InGaAsN quantum wells by means of composition-sensitive high-resolution transmission electron microscopy and photoluminescence. In as-grown samples, we find In-concentration fluctuations of ±5% on a length scale of 20 nm in a two-dimensional grown quantum well. No indications for N concentration fluctuations are found within the limits of resolution. Annealing homogenizes the In distribution within the well and causes diffusion of N out of the quantum well. According to our compositional analysis, the blueshift in the photoluminescence can in part be attributed to reduction in N concentration inside the well. The more homogeneous In distribution leads to a reduction in linewidth and Stokes shift. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1509122]

InGaAsN is a solid solution with a large size mismatch of the constituents on the group-V sublattice. This size mismatch leads to a number of unusual optical properties,[1–5] e.g., a strong band gap bowing, a large. Stokes shift between absorption and emission,[5] and a blueshift of the emission with increasing excitation power. N incorporation into InGaAs beyond about 1% causes strong quenching of the luminescence and a broadening of the luminescence linewidth.[2] Postgrowth annealing, however, can improve the optical properties significantly (i.e., can increase the PL intensity by a factor of up to 20 and reduce the spectral linewidth) but leads to a blueshift of the photoluminescence (PL) peak.[6–9]

Little is known up until now about the structural origin of these effects of annealing. Several possibilities can be imagined, e.g., a change in (i) well width, (ii) strain, and (iii) composition (concerning both In and N) or any combination of them. In a previous study, we have shown that clarification is possible by the direct analysis of the In and N contents by high-resolution transmission electron microscopy.[10] In the present letter, we compare the structural and compositional properties (TEM) of as-grown and annealed InGaAsN quantum wells and relate them to the optical properties The observed improvement in optical properties upon annealing can be related to a homogenization of the In distribution in the quantum well. No indications for N clustering are found within the achievable resolution before and after annealing.

A stack of five InGaAsN quantum wells is grown by plasma-assisted molecular-beam epitaxy at 450 °C substrate temperature (for details of the growth process see Ref. 11). The quantum wells in this study have a nominal thickness of 6.2 nm, a nominal atomic concentration of $x = 0.36$ In and $y = 0.019$ N. The wells are separated by 27 nm thick GaAs barriers. The as-grown sample has been divided into two parts. One part was annealed at a temperature of 720 °C for 10 min to improve the optical properties. For PL measurements, the samples were excited with a titanium–sapphire laser tuned to 790 nm. PL and PL excitation spectra were recorded at 7 K and at 300 K.

From both as-grown and annealed samples, cross-sectional samples were prepared in [100] projection for TEM by subsequent mechanical grinding and polishing and ion milling with 4 keV Ar^+ ions to achieve electron transparency. High-resolution TEM has been performed in a Philips CM 300UT microscope which has a point resolution of 0.165 nm when operated at 300 kV. The In and N distributions in these samples were analyzed by a combined evaluation (i) of the tetragonal lattice distortion of the unit cell obtained from experimental high-resolution micrographs, and (ii) of the intensity, I_{002}, of the chemically sensitive (002) reflection in respective dark-field images of the identical areas. This analysis yields data pairs of lattice distortion and dark-field intensity with high spatial resolution. Each data pair can be converted into a data pair of In and N (for the detailed procedure, see Refs. 10 and 12), i.e., we obtain separate values for the local N and In concentrations. Dark-field micrographs were taken close to high-resolution transmission electron micrographs exactly in the ⟨100⟩ zone axis. The quantitative analysis of the dark-field intensities I_{002} utilized direct recording on a charge coupled device (CCD) 1024×1024 pixels 12-bit camera mounted on the TEM.

Figure 1 shows low-temperature (7 K) PL and PL excitation spectra of the sample before and after annealing. The PL of the as-grown quantum wells shows a peak at 0.93 eV, which is highly asymmetric with a broad wing in the low-energy region centered around 0.84 eV. The comparison of the photoluminescence peak with the PL excitation spectrum indicates a Stokes shift of about 70 meV. After annealing, the peak intensity of the quantum well emission is increased by a factor of 20 and shows a blueshift of approximately 70

[a]Electronic mail: martin.albrecht@ww.uni-erlangen.de

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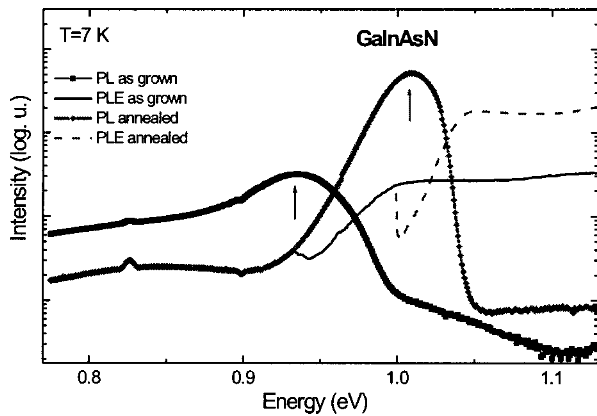

FIG. 1. PL spectra at 7 K of the InGaAsN/GaAs quantum wells as grown (continuous line) and annealed (dotted line).

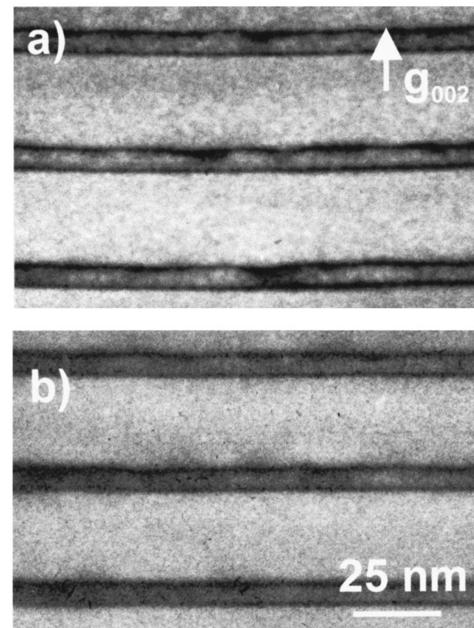

FIG. 2. Dark-field image using the (002) reflection of the sample before (a) and after annealing (b). Looking at the glancing angle along the quantum well, strong fluctuations in dark-field contrast on a length scale of 20 nm can be seen in (a), while the contrast inside the well is more homogeneous in (b).

meV from 0.94 to 1.01 eV. The spectral linewidth is decreased from 80 to 30 meV, the Stokes shift is reduced to 40 meV. The low-energy wing is now clearly separated from the quantum well emission and forms a broad band. The intensity in this band is lower by almost one order of magnitude.

Figure 2 shows a comparison between (002) dark-field images of the sample before and after annealing. The quantum wells can be seen as dark stripes between even darker horizontal lines, i.e., by a reduced dark-field intensity I_{002}. The dark horizontal lines occur due to a combined action of In and N composition leading to $I_{002}=0$. The as-grown samples exhibit pronounced lateral fluctuations of I_{002} along the quantum well, whereas the annealed sample does not. It is to be noted that the thickness of both as-grown and annealed quantum wells, as marked by the horizontal parallel lines, does not fluctuate. Table I quantifies dark-field intensities and strain values, fluctuation amplitudes and the In and N concentrations deduced from them.

In principle, these observed dark-field fluctuations can be due to fluctuations in the In or N concentrations or both. From the comparison of the tetragonal distortion with the dark-field intensity, we find that areas with an increased dark-field intensity exhibit an increased lattice distortion while areas with a reduced dark-field intensity show a reduced lattice distortion. Quantitative analysis yields that the fluctuations in dark-field intensity are caused by fluctuations in In concentration, while the N concentration stays constant. From the analyses of a number of such sites, we obtain a lateral In fluctuation of ± 0.05 in as-grown samples and ± 0.01 in annealed samples.

In order to determine the In and N profiles across the wells we smoothened the data by averaging along the well over a length of 50 nm. The In and N profiles, as calculated from these data, are shown in Figs. 3(a) and 3(b). They are symmetric in the as-grown samples and show a nearly Gaussian shape. The maximum In concentration is about 33%, the maximum N concentration is about 3.0%. The width of the N and In distributions is 7.4 nm which corresponds well to the intended thickness of the quantum well. After annealing, the In profile has changed only slightly. The maximum In concentration is now 31%, the thickness is now 8.5 nm. The N concentration profile, however, broadens to 10.3 nm. In particular, the N concentration in the center of the well is reduced to 2%. From Fig. 3(b), we should note that there is a tendency of N segregation toward the interfaces. However, the observed fluctuation of N within the well is within the achievable accuracy of our method (i.e., below 0.1%).[10]

Based on our structural analysis, we may now draw some conclusions on the observed changes in optical properties upon annealing, i.e., (i) the blueshift of the quantum well emission, (ii) the reduction in linewidth, and (iii) the reduction in intensity of the pronounced low-energy wing.

(i) Our compositional analysis yields two main contributions to the observed blueshift in emission: N diffusion out of the quantum well and the dissolution of In-rich inclusions present in the as-grown quantum well structures. These processes result in a reduction of the maximum In concentration and thus in a re-

TABLE I. Summary of experimental results and evaluations. Values in brackets indicate the observed fluctuations.

	I_{002} intensity (fluctuation)	strain (fluctuation)	In concentration (fluctuation)	N concentration	Length-scale of In fluctuation (nm)
As grown	0.52 (±0.17)	0.015 (±0.004)	0.33 (±0.05)	0.030	20±7
Annealed	0.32 (±0.10)	0.017 (±0.002)	0.31 (±0.01)	0.02	25±3

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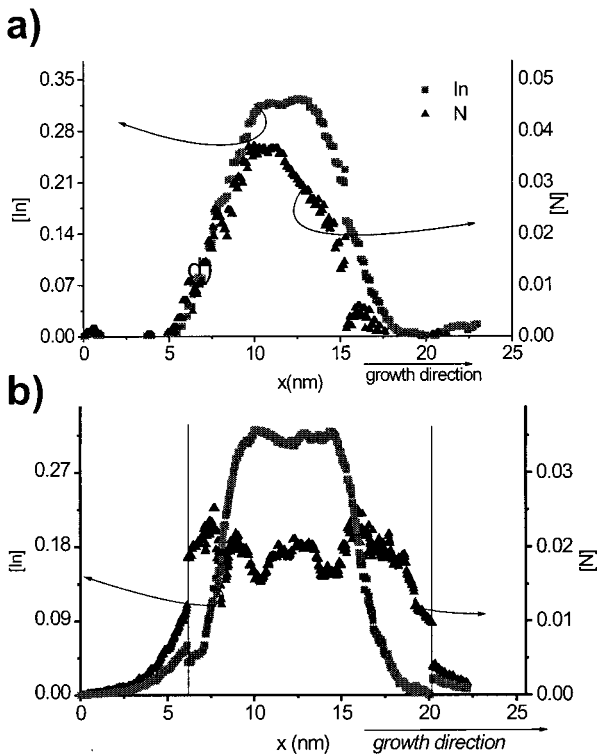

FIG. 3. In and N profiles before (a) and after (b) annealing as calculated from (002) dark-field intensity and strain profiles.

moval of deep localizing potential fluctuations. Because of the lack of reliable data (like band offset, band gap bowing), it is premature at the moment to quantify the experimentally analyzed changes in strain, composition, and size distribution of In clusters on the optical transitions. On the other hand, a rough estimation based on published data of quantum wells of the same thickness shows that the main part in the blueshift can be attributed to the reduction in N concentration.[13]

(ii) Our measurements clearly show that the reduction in PL linewidth and in Stokes shift is related to the homogenization of the In distribution. This result indicates that at least a part of the localization phenomena found in InGaAsN quantum wells can be explained by In concentration fluctuations. The homogenization of the In distribution leads to a reduction of areas with lower localization energy and the optical behavior is close to that of an ideal quantum well. Since our analysis shows a homogeneous N concentration in both as-grown and annealed samples (within the limits of resolution of 2 nm), we assume N to influence optical spectra only on the scale of statistical alloy fluctuations or by short-range order effects[14] rather then by clustering and phase separation.

(iii) The pronounced low-energy band (centered around 0.82 eV) in the low-temperature PL of as-grown samples is clearly reduced after annealing. From the reduction of these transitions with the decrease in In-concentration fluctuations, one might conclude that these transitions are due to In-rich inclusions. However, a similar PL and TEM based analysis of annealed samples with different In concentrations between 10% and 30%[15] shows that the intensity of these transitions increases with decreasing In concentration. Moreover, the peak energy of these transitions remains fixed and is independent of the In or N concentrations. These observations point toward an atomic defect of an intrinsic or extrinsic nature. Pomarico *et al.*[16] relate these transitions to C or Zn acceptors. Another explanation could be due to an intrinsic atomic defect or defect complex (e.g., $As_{Ga}-N_{As}$, or N–N, and N–As split interstitials).[17]

In summary, we find from a quantitative high-resolution TEM analysis that deep localizing potential fluctuations in InGaAsN grown by molecular-beam epitaxy are mainly caused by In concentration. We find no indications for thickness fluctuations. N clustering is absent, which is in good accordance with work by McKay *et al.*[18] Annealing leads to homogenization of the In concentration and to diffusion of N out of the quantum well. The blueshift of the PL on annealing in our samples is caused by reduced N and In concentrations. Our measurements confirm results by Pinault and Tournier[3] who concluded from a comparison between GaAsN and InGaAsN quantum wells that N *per se* has no impact on the observed deep carrier localization in InGaAsN quantum wells.

[1] L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Duvaut, C. Vanuffel, A. Million, and A. Chenevas-Paule, Appl. Phys. Lett. **76**, 2241 (2000).
[2] A. Kaschner, T. Lüttgert, H. Born, A. Hoffmann, A. Y. Egorov, and H. Riechert, Appl. Phys. Lett. **78**, 1391 (2001).
[3] M.-A. Pinault and E. Tournié, Appl. Phys. Lett. **78**, 1562 (2001).
[4] A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 195320 (2001).
[5] T. Makimoto, H. Saito, T. Nishida, and N. Kobayashi, Appl. Phys. Lett. **70**, 2984 (1997).
[6] Z. Pan, L. H. Li, W. Zhang, Y. W. Lin, R. H. Wu, and W. Ge, Appl. Phys. Lett. **77**, 1280 (2000).
[7] Z. Pan, T. Miyamoto, S. Sato, F. Koyama, and K. Iga, Jpn. J. Appl. Phys., Part 1 **38**, 1012 (1999).
[8] X. Yang, J. B. Heroux, M. Jurkovic, and W. I. Wang, J. Vac. Sci. Technol. B **17**, 1144 (1999).
[9] T. Kitatani, K. Nakahara, M. Kondow, K. Uomi, and T. Tanaka, J. Cryst. Growth **209**, 345 (2000).
[10] V. Grillo, M. Albrecht, T. Remmele, H. P. Strunk, A. Y. Egorov, and H. Riechert, J. Appl. Phys. **90**, 3792 (2001).
[11] A. Y. Egorov, D. Bernklau, B. Borchert, S. Illek, D. Livshits, A. Rucki, M. Schuster, A. Kaschner, A. Hoffmann, G. Dumitras, M. C. Amann, and H. Riechert, J. Cryst. Growth **227**, 545 (2001).
[12] The tetragonal distortion is given by $\varepsilon = 2\, c_{12}/c_{11}\, a_{\mathrm{InGaAsN}} - a_{\mathrm{GaAs}}/a_{\mathrm{GaAs}}$, where a_{InGaAsN} and a_{GaAs} are the lattice constants of InGaAsN and GaAs, respectively. The dark-field intensity is given by $I_{002} = A^2 = k^2|f_{\mathrm{III}} - f_{\mathrm{V}}|^2$ and depends on the difference of the atomic scattering factors of the chemical species ($f_{\mathrm{III}} = x(f_{\mathrm{In}} - f_{\mathrm{Ga}}) + f_{\mathrm{Ga}}$; $f_{\mathrm{V}} = y(f_{\mathrm{N}} - f_{\mathrm{As}}) + f_{\mathrm{As}}$); k is a constant. The lattice distortion is analyzed with the DALI programme package. Theoretical curves of the dark-field intensities for InGaAsN are obtained by Block wave calculations with the EMS programme package (for procedures, see Ref. 10).
[13] Our estimations are based on the data published by Egorov *et al.* (Ref. 12). We assume a band gap bowing parameter of 12 eV for GaAsN and 0.8 eV for InGaAs. For the observed reduction in In concentration, we obtain a blueshift of 30 meV. The N contributes about 40 meV.
[14] P. R. C. Kent and Alex Zunger, Phys. Rev. Lett. **86**, 2613 (2001).
[15] A. Kaschner, A. Hoffmann, M. Albrecht, T. Remmele, V. Grillo, H. P. Strunk, A. Y. Egorov, and H. Riechert (unpublished).
[16] A. Pomarico, M. Lomascolo, R. Cingolani, A. Y. Egorov, and H. Riechert, Semicond. Sci. Technol. **17**, 145 (2002).
[17] S. B. Zhang and S. H. Wei, Phys. Rev. Lett. **86**, 1789 (2001).
[18] H. A. McKay, R. M. Feenstra, T. Schmidtling, and U. W. Pohl, J. F. Geisz, J. Vac. Sci. Technol. B **19**, 1644 (2001).

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