Inst. Phys. Conf. Ser. No 180
Paper presented at Microsc. Semicond. Mater. Conf., Cambridge, 31 March – 3 April 2003

In distribution in InGaN quantum wells: influence of phase separation, In segregation and In desorption

D Gerthsen, E Hahn, V Potin, A Rosenauer, B Kuhn[1], J Off[1], F Scholz[1], A Dussaigne[2] and N Grandjean[2]

Laboratorium für Elektronenmikroskopie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany
[1] 4. Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart, Germany
[2] Centre de Recherches sur l'Hétéro-Epitaxie et ses Applications, Rue B. Grégory, Sophia Antipolis, 06560 Valbonne, France

ABSTRACT: The local In distribution in InGaN quantum wells was measured in samples which were grown by metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) varying systematically the metal-flux ratio and the growth rate. The composition analyses were performed by local lattice parameter measurements based on lattice-fringe transmission electron microscopy (TEM) images. Composition fluctuations are observed in all samples on two typical scales: In-rich clusters with lateral sizes below 5 nm with high In concentration and weaker composition fluctuations on a 100 nm scale. The size of the clusters does not depend on the growth conditions, but the amplitude of the composition fluctuations is influenced by the growth rate. In-concentration profiles along the growth direction show the effect of In desorption and In segregation during the growth.

1. INTRODUCTION

It has already been shown some years ago that composition fluctuations in InGaN play a key role in the high emission efficiency of optoelectronic devices based on InGaN/GaN heterostructures (Chichibu et al 1998). Therefore, it is of considerable interest to measure the In concentration in InGaN quantum wells (QWs). Mappings of the In distribution at high spatial resolution can be obtained by energy dispersive X-ray analysis or electron energy loss spectroscopy in a transmission electron microscope as shown by Narukawa et al (1997) and Cho et al (2001). However, due to QW thicknesses of less than 5 nm, an analytical technique with an even better spatial resolution is desirable. Kisielowski et al (1997) presented composition analyses based on high-resolution (HR) TEM images, which showed composition fluctuations on a scale of only a few nanometers.

In this work, the In distribution of InGaN/GaN heterostructures grown by MOVPE and MBE using different metal-flux ratios and growth rates for the InGaN growth is quantitatively analysed by evaluating local lattice parameters using the DALI (digital analysis of lattice image) program package (Rosenauer et al 1996).

2. EXPERIMENTAL TECHNIQUES

A series of MOVPE samples was grown on SiC(0001) substrates using trimethylindium (TMIn), triethylgallium (TEGa), trimethylaluminium (TMAl) and NH_3 as precursors. After the growth of a 800 nm $Al_{0.12}Ga_{0.88}N$/1300nm GaN thick buffer layer at 1120°C, 3 nm InGaN and a 15 nm GaN cap layer were deposited at a substrate temperature T_s of 720°C. The precursor was switched from H_2 to N_2 for the InGaN and GaN cap layer growth. Keeping all other parameters constant, the TEGa and TMI fluxes were varied during the InGaN growth according to Table 1 in §3.

The effect of different growth rates was analysed with respect to the strength of the composition fluctuations. The investigated MOVPE samples consist of a SiC(0001) substrate, a 600 nm Si-doped $Al_{0.1}Ga_{0.9}N$ buffer layer and an undoped cap layer system containing 78 nm GaN, 240 nm $Al_{0.1}Ga_{0.9}N$ and 38 nm GaN. The InGaN QWs were grown at T_s = 670 °C at growth rates of 2.5 nm/min and 7.5 nm/min.

The MBE samples were grown on $Al_2O_3(0001)$ substrates. After the growth of a 25 nm GaN buffer layer at T_s = 500°C and a thick GaN layer (800°C, thickness between 2.5 and 6 μm), a thin InGaN quantum well (QW) was deposited T_s = 530°C. The InGaN was capped by 30 nm GaN after a growth interruption and increase of T_s up to 800°C. The In and Ga fluxes were varied under N-rich conditions by changing the MBE source temperatures which are given in Table 3.

The TEM investigations were carried out using a Philips CM200 FEG/ST microscope with a spherical aberration coefficient of 1.2 mm and a defocus spread of 7 nm. The local In concentration was determined by the measurement of local (0002) plane distances using the DALI program package taking into account the tetragonal strain of the InGaN strained-layer QWs and the elastic relaxation due to the thin TEM sample. It was shown by image simulations (Gerthsen et al, 2003) that two-beam lattice fringe images, which are taken by strongly exciting the 0004 reflection, centering the 0002 reflection on the optic axis and transmitting only the 0000 and 0002 reflections through the aperture, yield reliable results within large defocus and samples thickness ranges. In addition to the local In distribution, mean In concentrations were determined for each evaluated image which were again averaged to obtain an overall average In concentration $\bar{x}_{In}$. The standard deviation of $\bar{x}_{In}$ characterizes In-concentration fluctuations on a scale corresponding to the width of the evaluated images in the order of some 10 nm, which will be considered as large-scale fluctuations.

3. EXPERIMENTAL RESULTS

Fig.1(a) shows a grey-scale coded map of the local In distribution of sample VPE 14/100 (Table 1) which is representative for all MOVPE samples. In-rich clusters are observed with lateral sizes below 5 nm. The In-concentration profile plotted as a function of the (0002) plane (monolayer ML) number in [0001] direction shows a steep increase of the In concentration at the lower interface and a gradual decrease towards the GaN cap layer.

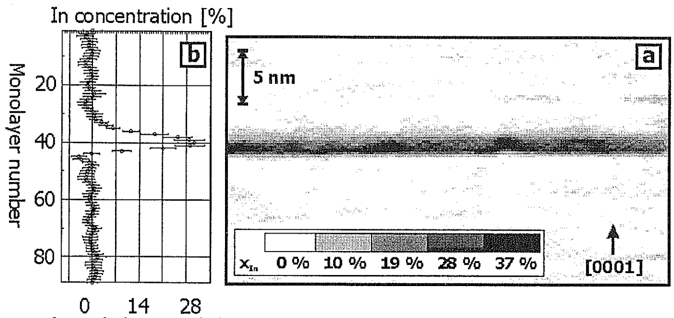

Fig.1(a) Grey-scale coded map of the local In concentration, (b) In concentration averaged along each ML and plotted as a function of the ML number in growth direction.

Table 1 contains the overall average In concentrations $\bar{x}_{In}$ and measured QW thickness as a function of the TEGa and TMIn fluxes. If the TMIn flux is increased by a factor of 1.7 at a constant TEGa flux (samples VPE 14/70, VPE 14/120), $\bar{x}_{In}$ increases only slightly. However, higher $\bar{x}_{In}$ are obtained if the TEGa flux is raised by a factor of 3.8 at a constant TMIn flux (samples VPE 14/70, VPE 54/70). Standard deviations for $\bar{x}_{In}$ between 2.2 and 4.9 % indicate that large-scale fluctuations are present in addition to the small In-rich clusters.

Samples	TEGa [sccm]	TMIn [sccm]	$\bar{x}_{In}$ [%]	In content [ML]	QW thickness [nm]
VPE 14/70	14	70	18.2 ± 4.9	1.6 ± 0.7	2.7 ± 0.5
VPE 14/100	14	100	18.8 ± 3.4	1.8 ± 0.4	2.9 ± 0.5
VPE 14/120	14	120	19.6 ± 2.2	2.2 ± 0.3	3.2 ±0.5
VPE 41/70	41	70	21.9 ± 3.2	2.6 ± 1.6	2.9 ± 0.6
VPE 54/70	54	70	23.8 ± 6.1	2.7 ± 1	3.5 ± 1.5

Table 1. Dependence of the average In concentration $\bar{x}_{In}$ and measured QW thickness on the TEGa and TMIn fluxes for the MOVPE-grown samples. The errors correspond to the standard deviation.

The effect of the growth rate variation on the In distribution and In incorporation are visualized in Table 2. In addition to $\bar{x}_{In}$ and the QW thickness, the average In concentration of the In-rich clusters was determined. The decrease of the standard deviations for $\bar{x}_{In}$ and $\bar{x}_{In,cluster}$ is a clear indication for the homogenization of In distribution in the sample grown at a higher rate.

Growth rate	$\bar{x}_{In}$ [%]	QW thickness [nm]	$\bar{x}_{In,cluster}$ [%]
2.5 nm/min	16 ± 6	1.5 ± 0.2	46 ± 24
7.5 nm/min	12 ± 2	2.0 ± 0.4	27 ± 8

Table 2: Dependence of the overall average In concentration $\bar{x}_{In}$, QW thickness and averaged In concentration of the clusters $\bar{x}_{In,cluster}$ on the InGaN growth rate.

Fig.2 displays a representative example for the local In distribution of the InGaN QWs in the MBE samples and the corresponding In-concentration profile along the growth direction. In-rich clusters with small sizes are observed as for the MOVPE samples. However, the In-concentration profile along the growth direction is characterized by a diffuse lower interface and a steep decrease of the In concentration towards the cap layer. The maximum In concentration is located approximately in the center of the QW, which can be also observed in Fig.2(a), in contrast to the MOVPE samples where the maximum In concentration is located close to the lower interface (Fig.1).

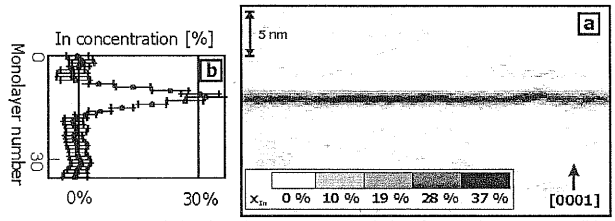

Fig.2(a) Grey-scale coded map of the local In concentration of sample MBE 4, (b) In concentration averaged along each ML and plotted as a function of the ML number in growth direction.

The measured QW thickness and $\bar{x}_{In}$ for the MBE samples are given in Table 3 as a function of the Ga and In source temperatures which determine the Ga and In fluxes. For the MBE growth, the increase of the In flux or Ga flux leads - as expected - to higher In concentrations or Ga concentrations respectively.

Samples	T Ga [°C]	T In [°C]	$\bar{x}_{In}$ [%]	In content [ML]	QW thickness [nm]
MBE 1	800	710	19.3 ± 4.6	1.5 ± 0.2	2.5 ± 0.4
MBE 2	800	720	21.8 ± 4.3	2.0 ± 0.4	3.0 ± 0.4
MBE 3	820	720	19.2 ± 5.9	1.6 ± 0.4	2.4 ± 0.3
MBE 4	830	720	17.4 ± 5.1	1.7 ± 0.4	3.1 ± 0.7

Table 3: Dependence of the average In concentration and measured QW thickness on Ga and In fluxes expressed by the source temperatures during the MBE growth.

4. CONCLUSIONS

Several conclusions can be drawn from our experimental results, which are summarized by the following points.

1. Pronounced composition fluctuations are always present in InGaN independent of the growth technique (MBE or MOVPE) and particular set of growth parameters. Composition fluctuations are even observed at small average In concentrations below 5 % (Schowalter et al 2001). It is plausible to assign the inhomogeneous In distribution to phase separation due to the large miscibility gap that has been predicted for InGaN (Ho and Stringfellow 1996).
2. Composition fluctuations occur on two typical scales:
   - small In-rich clusters with lateral extensions of less than 5 nm and high In concentrations
   - weaker composition fluctuations on a scale of a some 10 nm to 100 nm, which are "superimposed" on the In-rich clusters.
3. The size of the In-rich clusters could not be significantly modified by the variation of the growth parameters. However, the increase of the growth rate leads to a lower average In concentration in the clusters (Table 2) indicating that kinetics plays a role in their formation and a general homogenization of the In distribution.
4. The In incorporation during the MOVPE growth does not improve if the TMIn/TEGa flux ratio is increased in the investigated range of growth conditions at generally high $\bar{x}_{In}$ around 20 %. The increase of $\bar{x}_{In}$ at higher TEGa fluxes (samples VPE 41/70 and 54/70, Table 1) is attributed to reduced In desorption during the growth. The dependence of the $\bar{x}_{In}$ on the In and Ga fluxes during MBE growth (Table 3) exhibits the intuitively expected behavior.
5. The In-concentration profiles along the growth direction Fig.1(b) and Fig.2(b) were evaluated according to Muraki et al (1992). In segregation coefficients can be determined which describe the segregation probability of the indium atoms from the uppermost crystalline layer into the floating layer on the growth surface. In segregation leads to a gradually increasing In-concentration at the lower QW interface. The indium that accumulates in the floating layer during the InGaN growth is incorporated during the GaN cap layer growth. As a result, an asymmetrical In-concentration profile is obtained as shown in Fig.1(b). In contrast, the shape of the In-concentration profile of the MBE sample Fig.2(b) exhibits a more gradual increase of the In concentration at the lower interface and a rather abrupt upper interface. The latter can be explained by In desorption during the growth interruption after the InGaN deposition when T_s is increased from 530 °C to 800 °C. A smaller segregation probability R = 0.69 is obtained for the MOVPE samples in contrast to R = 0.85 for the MBE samples despite higher T_s values during the MOVPE growth. However, it has to be noted that the In segregation probabilities depend sensitively on the growth conditions, in particular the III/V-flux ratio (Chen et al 2001). Further details on the evaluation of the In-concentration profiles are given by Potin et al (2003).

ACKNOWLEDGEMENTS

We thank Dr. Y. Kobayashi (NTT BRL, Atsugi, Japan) who has significantly contributed to the growth of the MOVPE samples. The financial support by the Deutsche Forschungsgemeinschaft (DFG) and the Bundesministerium für Bildung and Forschung (BMBF, Germany) is gratefully acknowledged.

REFERENCES

Chen H, Feenstra R M, Northrup J E, Zywietz T and Neugebauer J 2001 MRS Internet J. Nitride Res. **6**, 11

Chichibu S, Sota T, Wada K, and Nakamura S 1998 J. Vac. Sci. Technol. B **16**, 2204

Cho H K, Lee J Y, Sharma N, Humphreys C, Yang G M, Kim C S, Song J H Yu P W 2001 Appl. Phys. Lett. **79**, 2594

Gerthsen D, Hahn E, Neubauer B, Potin V, Rosenauer A, and Schowalter M 2003 phys. stat. sol. (c), submitted

Ho I-Hsiu and Stringfellow G B 1996 Appl. Phys. Lett. **69**, 2701

Kisielowski C, Liliental-Weber Z, and Nakamura S 1997 Jpn. J. Appl. Phys. **36**, 6932

Muraki K, Fukatsu S, Shiraki Y, and Ito R 1992 Appl. Phys. Lett. **61**, 557

Narukawa Y, Kawakami Y, Funato M, Fujita S, and Nakamura S 1997 Appl. Phys. Lett. **70**, 981

Potin V, Hahn E, Rosenauer A, Gerthsen D, Kuhn B, Scholz F, Dussaigne A, Damilano B, and N Grandjean 2003 J. Crystal Growth, submitted

Rosenauer A, Kaiser S, Reisinger T, Zweck J, Gebhardt W, and Gerthsen D 1996 Optik **102**, 63

Schowalter M, Neubauer B, Rosenauer A, Gerthsen D, Schön O and Heuken M 2001 Mat. Res. Soc. Online Symp. Proc., spring meeting 2001, Symposium E, paper E 3.6, http://www.mrs.org/epubs/proceedings/spring2001/