

Incorporation of indium during molecular beam epitaxy of InGaN

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We report on the incorporation of In during growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ by molecular beam epitaxy under varying In/Ga flux ratios and with different film thicknesses. The incorporation efficiency studied by energy dispersive x-ray microanalysis, high-resolution x-ray diffraction and photoluminescence spectroscopy is strongly affected by the chosen fluxes of Ga and N and is limited by the excess of nitrogen compared to gallium. Furthermore, thick films exhibit a decrease of the In content in growth direction. The behavior can be explained by considering the different stabilities of the two binary compounds InN and GaN. © 1998 American Institute of Physics.

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The development of blue light emitting diodes¹ and laser diodes² has focused a lot of research activity on the growth of GaN-based III-V nitrides. Particularly, $\text{In}_x\text{Ga}_{1-x}\text{N}$ has raised a lot of interest for use in the active region of these devices, as the band gap of this material can be varied over nearly the whole spectral range.³

The growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ is complicated by the lattice mismatch and the different thermal stabilities of the two constituents InN and GaN. The lattice mismatch leads to a miscibility gap,^{4,5} which can cause fluctuations of the In content across the film. Evidence for phase separation was reported recently for thick $\text{In}_x\text{Ga}_{1-x}\text{N}$ films⁶ as well as for annealed multiple quantum wells.⁷ Furthermore, the lattice mismatch results in a thickness dependence of the composition in strained heterostructures grown by metal vapor phase epitaxy⁸ and in the generation of misfit dislocations due to lattice relaxation. The different binding energies of InN and GaN are reflected in their decomposition temperatures. It has been shown that the decomposition of InN starts at approximately 630 °C, whereas GaN is stable up to 850 °C under vacuum.⁹ Consequently, loss of In from the film not only occurs due to the reevaporation from physisorbed surface states but also due to the thermal decomposition of InN bonds. Both lead to the formation of In droplets on the surface, which entrap impinging In atoms, thus reducing the amount of In available for incorporation in the film. Since the size and the density of the droplets increase during growth, the average In content shows a vertical gradient in the film. Moreover, the droplets disturb the homogeneous distribution of In and Ga atoms across the growth surface and are an additional source for the commonly observed fluctuations of the In content.^{10,11}

The scope of this study was to find experimental evidence for the effects described above for the case of molecular beam epitaxy (MBE) through the correlation of the In incorporation with growth parameters. In particular, the dependence of the composition on the film thickness and the

fluxes of In, Ga and N was investigated. The present letter is restricted to the variation of the average In content of the films; lateral fluctuations of the local composition will be discussed elsewhere.^{11,12}

The InGaN layers were grown on *c*-plane sapphire substrates covered with a 30 nm thick GaN layer in a standard MBE system using conventional effusion cells for Ga and In. Nitrogen was supplied through a radio frequency plasma source allowing growth rates of approximately 600 nm/h. All fluxes were calibrated by the growth rates of GaAs, GaN or metallic In. The substrate temperature was 650 °C, and the substrates were nitridated for 12 min at this temperature prior to growth. The samples were characterized *in situ* and *ex situ* utilizing reflection high-energy electron diffraction (RHEED), high-resolution x-ray diffraction (HRXRD), photoluminescence spectroscopy (PL) at 4.2 K, transmission electron microscopy (TEM) and energy dispersive x-ray microanalysis (EDX).

To investigate the dependence of the composition on the incident fluxes, several samples were grown with different In fluxes while keeping the fluxes of Ga and N constant. The Ga and N fluxes were 6.5 and 8.3 $\text{nm}^{-2} \text{s}^{-1}$, respectively, and the In flux was varied between 1.6 and 16 $\text{nm}^{-2} \text{s}^{-1}$. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ films had a thickness of 600 nm, so that the films are fully relaxed. Figure 1 shows the variation of the average In content with the In flux as determined from HRXRD measurements of the (0002) reflection. For low In fluxes the average In content increases linearly as expected. The slope corresponds to an In sticking coefficient of $s_{\text{In}} = 0.16 \pm 0.05$, s_{In} being the ratio of incorporated to offered In atoms. The low sticking coefficient can be understood by considering the different binding energies of the two binaries. While GaN is stable at the growth temperature of 650 °C, InN is not. Consequently, the Ga sticking coefficient is unity as long as the N flux exceeds the Ga flux, whereas the In sticking coefficient is significantly smaller. For higher In fluxes, above approximately 8 $\text{nm}^{-2} \text{s}^{-1}$, the In content is limited to a value of $x_{\text{In}} \approx 0.2$. In this growth regime the N sticking coefficient is unity. Higher In contents would re-

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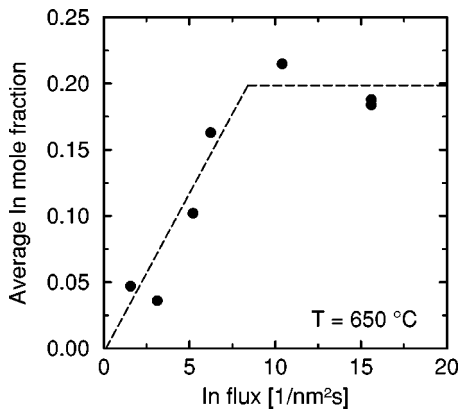


FIG. 1. The dependence of the composition on the In flux for constant Ga and N fluxes of 6.5 and 8.3 nm⁻² s⁻¹, respectively, as determined from HRXRD.

quire the formation of InN bonds in expense of GaN bonds, which is unlikely to occur due to the higher binding energy of GaN compared to InN. The maximum possible In content is thus determined by the excess N flux over the Ga flux:

$$x_{\max} = 1 - \frac{f_{\text{Ga}}}{f_{\text{N}}} \quad (1)$$

In the experiment shown, this value amounts to $x_{\max} = 0.21$, which agrees well with the data shown in Fig. 1. Therefore, according to Eq. (1) the Ga flux should be significantly lower than the N flux in order to achieve a high In content.

To obtain more information about the compositional inhomogeneity of the alloy we have grown a series of samples with thicknesses of the In_xGa_{1-x}N film ranging from 30 to 1000 nm. The fluxes of Ga and N were the same as in the previous experiment, and the In flux was held constant at 5.2 nm⁻² s⁻¹. All samples were cooled down after growth under a flux of activated nitrogen.

As can be seen in Fig. 2, the lattice constant c decreases with thickness, which one would also expect for the relaxation of a strained film. Therefore, the strain of the 100 nm thick In_xGa_{1-x}N sample was determined from the analysis of reciprocal space maps around the (10 $\bar{1}$ 5) reflection. This

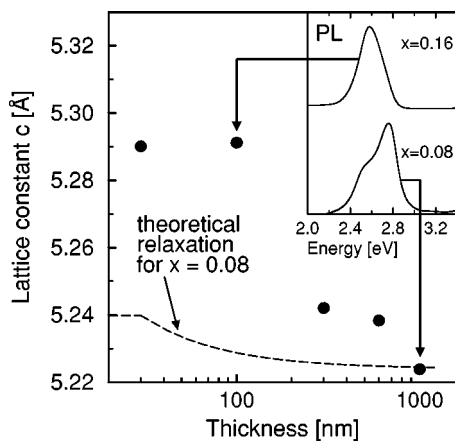


FIG. 2. The dependence of the lattice constant c on the thickness of the In_xGa_{1-x}N film. The inset shows the PL spectra taken at 4.2 K for the 100 and 1000 nm thick samples and the corresponding In mole fractions as determined from HRXRD considering the strain.

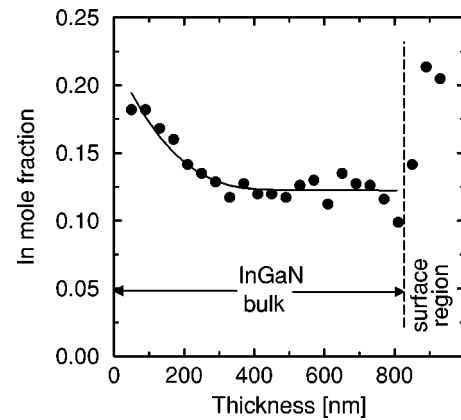


FIG. 3. The variation of the composition over the thickness as determined from the EDX microanalysis.

layer was found to be partially strained with an average In mole fraction of $x_{\text{In}} = 0.16$, whereas the 1000 nm thick epilayer had an In content of $x_{\text{In}} = 0.08$, assuming that this film is fully relaxed. To further estimate the influence of strain for samples grown under these conditions we calculated the critical thickness for an In mole fraction of $x_{\text{In}} = 0.08$ (Ref. 13) and determined the theoretical evolution of the lattice constant c due to relaxation of the structure if the composition was independent of the thickness.¹⁴ The result is shown as dashed curve in Fig. 2. From the comparison of this curve with the experimental values it can be concluded that the change in lattice constant is primarily caused by a variation of the composition with thickness rather than by relaxation. The change in composition can be explained by the formation of In droplets on the surface, as mentioned earlier. As the amount of In in the droplets depends on the growth time, the In content in the layer is also affected by the thickness, such that thinner films have a higher In content. It should be noted that this gradient in composition is primarily important for thicker layers, as the formation of droplets happens on a relatively long time scale. Thus, quantum well structures should not be significantly affected by this phenomenon. The inset of Fig. 2 shows the PL spectra of the 100 nm and the 1000 nm thick samples. The luminescence is relatively broad and shifts towards higher energies with increasing thickness confirming the different average compositions.

The thickness dependence of the composition is confirmed by EDX measurements of the 1000 nm thick sample. The EDX technique yields the local composition of a sample prepared for TEM by the analysis of the characteristic x-ray spectra of the elements after excitation with an electron beam. For a quantitative analysis the standardless thin film approximation was used utilizing calculated sensitivity factors. The values presented in Fig. 3 are the averaged In contents of horizontal line scans at different thicknesses.

The results are in good qualitative agreement with the HRXRD measurements discussed above. The In content is highest close to the substrate interface and it decreases monotonically up to a thickness of approximately 300 nm. For higher thicknesses the composition remains roughly constant within the experimental errors. In the region close to the surface one finds a steep increase of the In content, which is probably caused by the accumulation of In on the surface during growth. Two-dimensional EDX mappings show In-

rich clusters in this region, which appear to originate from single In droplets converted to $\text{In}_x\text{Ga}_{1-x}\text{N}$ with high In content during the cool-down procedure under a flux of activated nitrogen. This conversion of In droplets can also be observed *in situ* for samples grown under a high In flux, where the excess In covers the whole sample surface. In this case the RHEED pattern after growth is diffuse due to the In coverage and the spacing of the diffraction spots fits to the lattice constant of the underlying $\text{In}_x\text{Ga}_{1-x}\text{N}$. When cooling down under a flux of activated nitrogen below a temperature of approximately 500 °C the intensity of the diffraction pattern rises and the lattice constant changes to that of InN. An EDX analysis of one of these samples yielded an In mole fraction larger than $x_{\text{In}}=0.9$ at the surface.

In conclusion, it has been shown that the composition of $\text{In}_x\text{Ga}_{1-x}\text{N}$ thin films is significantly affected by the incident fluxes and the layer thickness. The In content is limited to a maximum value, determined by the chosen fluxes of Ga and N. Furthermore, the composition is strongly dependent on the thickness of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ film and decreases up to a thickness of approximately 300 nm. The low binding energy of InN compared to GaN, leading to the formation of In droplets on the growth surface, was proposed to be responsible for the observed effects.

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