Assessment of the short and long range homogeneity of MOVPE–grown InGaN epilayers

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Abstract

InGaN epilayers grown by MOVPE were investigated by micro–Raman spectroscopy, photoluminescence and spectrally–resolved cathodo–luminescence in order to analyse the indium distribution at the micro and macro scale. It was found that the In molar fraction increases from centre to edge of the 2" wafers. The Raman spectra of the ternary alloys exhibit additional In–related modes, with respect to GaN spectra. One of these Raman bands is tentatively ascribed to In clustering, further justified by CL spectral maps.

Introduction

InGaN/GaN hetero–structures are at the basis of many opto–electronic applications. For such applications both long and short range composition homogeneity is required. In this work we shall present the results of an extensive investigation on InGaN/GaN hetero–structures deposited by MOVPE on (0001) sapphire, using Ammonia, TMG and TMI precursors. The flow–dynamic conditions were carefully optimized in order to achieve a uniform layer thickness, but it was found that this condition is not sufficient to obtain homogeneus In incorporation. Composition profiles along the wafer radius were indeed detected by micro–Raman spectroscopy, spectrally resolved cathodo–luminescence (CL) and photoluminescence (PL). Generally the centre incorporates less indium than the periphery, however the composition profile is seen to change according to growth parameters (probably in connection with the MOVPE system flowdynamics). This information is a useful feedback for growth experiments. Furthermore, CL maps of the emission wavelength maximum suggests that local In clustering occurs.

Experimental

The growth of the InGaN layers was performed in a home–made MOVPE system using (0001) sapphire substrates and the standard Ammonia, TMG and TMI precursors. Typically the hetero–structure included a low–T GaN buffer (80–100 nm), a GaN layer deposited at high temperature (500–600 nm thick) and the InGaN layer deposited at 800–820 °C. In molar fraction was controlled either by changing the TMG/TMI flow ratio or by adding hydrogen into the reaction chamber. Micro–Raman measurements were carried out in backscattering geometry with a DILOR X–Y Micro–Raman spectrometer, using an Ar+ laser with line at 514.5 nm for excitation. Photoluminescence (PL) measurements were carried out both at room temperature and 12 K, using a He–Cd laser (line at 325 nm) for the excitation of the InGaN samples and a high–resolution monochromator for the analysis of the emitted light. Standard phototube and lock–in amplifier were used for signal detection. CL measurement were performed with an XiCLOne system from Gatan. The detection is done with a CCD camera, which allows a full spectral imaging, i.e. mapping of the spectral parameters of the selected luminescence band. The measurements were done at liquid nitrogen temperature (~80K). The spectra were typically obtained with an acceleration voltage of the e–beam of 5kV and beam current of 9nA, that give a spatial resolution around a few hundred nm.

Results and discussion

Figure 1a shows typical Raman spectra of InGaN alloys with different nominal In molar fractions, and a GaN reference spectrum which exhibits the typical allowed modes for hexagonal GaN in backscattering geometry: E_2 at 567 cm^{-1} and A_1(LO) at 734 cm^{-1}. The InGaN layers present additional bands at about 522, 560 and 680 cm^{-1}. The line at 560 cm^{-1} is ascribed to the E_2 mode of the ternary alloy and is observed to shift linearly with the x molar fraction of $In_xGa_{1-x}N$, within the range 0 – 0.18, as reported in Figure 1b. The broad band around 680 cm^{-1} is seen to increase with the In content, suggesting that this Raman feature is probably generated by In

clustering. These spectra agree with previous Raman studies on InGaN compunds [1].

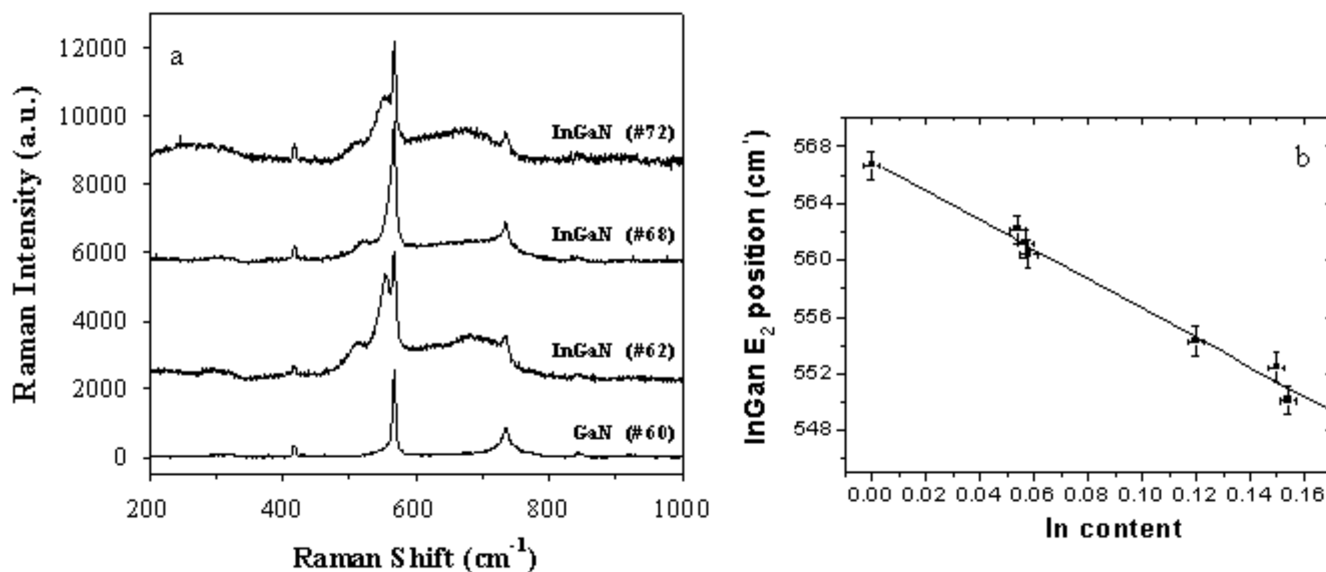

Fig 1: a) Raman spectra of GaN and InGaN layers, preset In content is 15 %, 6 % and 10% in samples 72, 68 and 62, respectively; b) Raman shift of the E_2 line in InGaN as a function of In content.

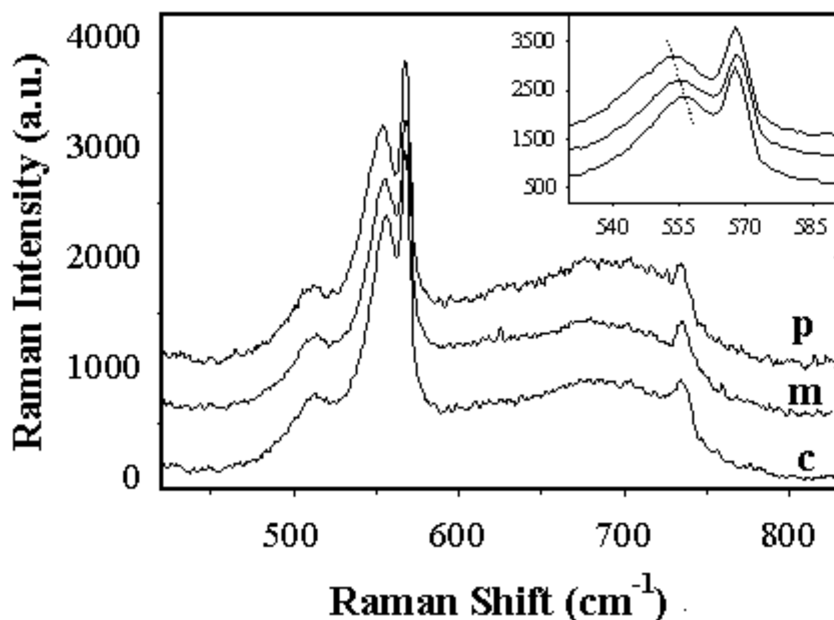

Fig.2: Raman spectra at the centre (c), mid–radius (m) and periphery (p) of sample #62 (10% In content)

In Figure 2 three Raman spectra collected at the centre, mid–radius and periphery of the layer # 62 are shown. The alloy–related band at ~550 cm^{-1} shifts to lower frequencies when moving from centre to periphery of the wafer. Considering what said above about Figure 1b, this shift suggests that the wafer periphery contains more

Indium than the centre.

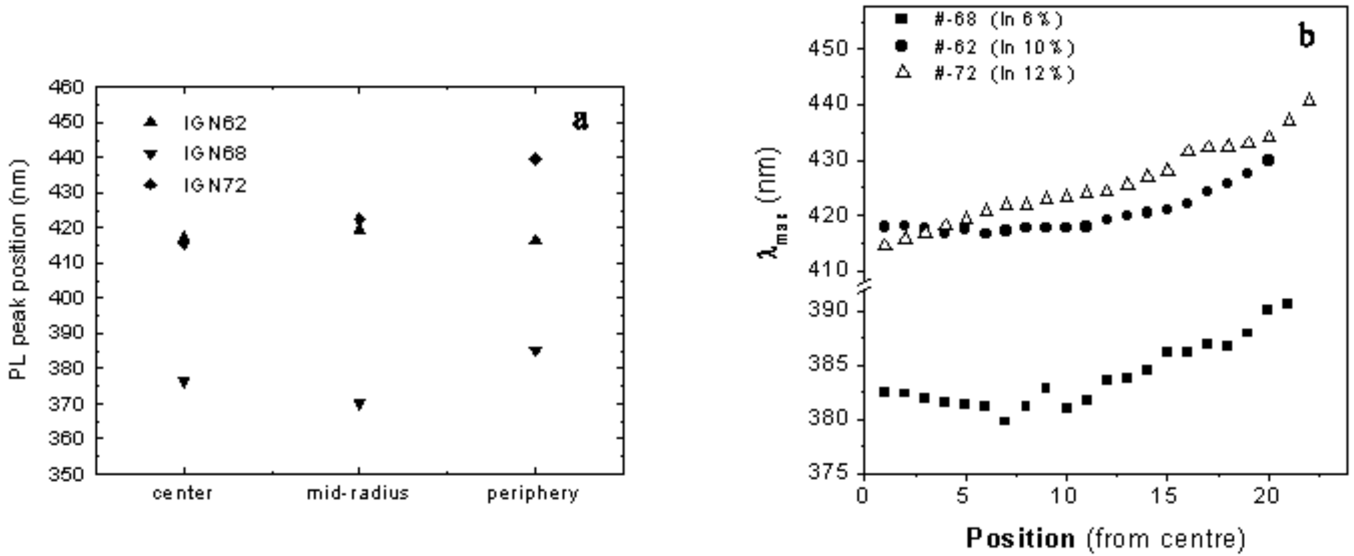

Fig.3: a) Band–band PL peak energy in different positions along the wafer diameter; b) CL profile of emission peak for the three samples

The composition gradient along wafer radius is confirmed also by PL and CL measurements. For example, the main band–band emission peak of PL spectra reveals that the material bandgap is generally smaller at the wafer periphery than in the centre, i.e.larger In fraction in the periphery (Figure 3a). The CL radial profiles of the peak wavelength for the same three samples show that the wavelength increase towards the wafer edge (Figure 3b), again indicating that In is more effectively incorporated in this area.

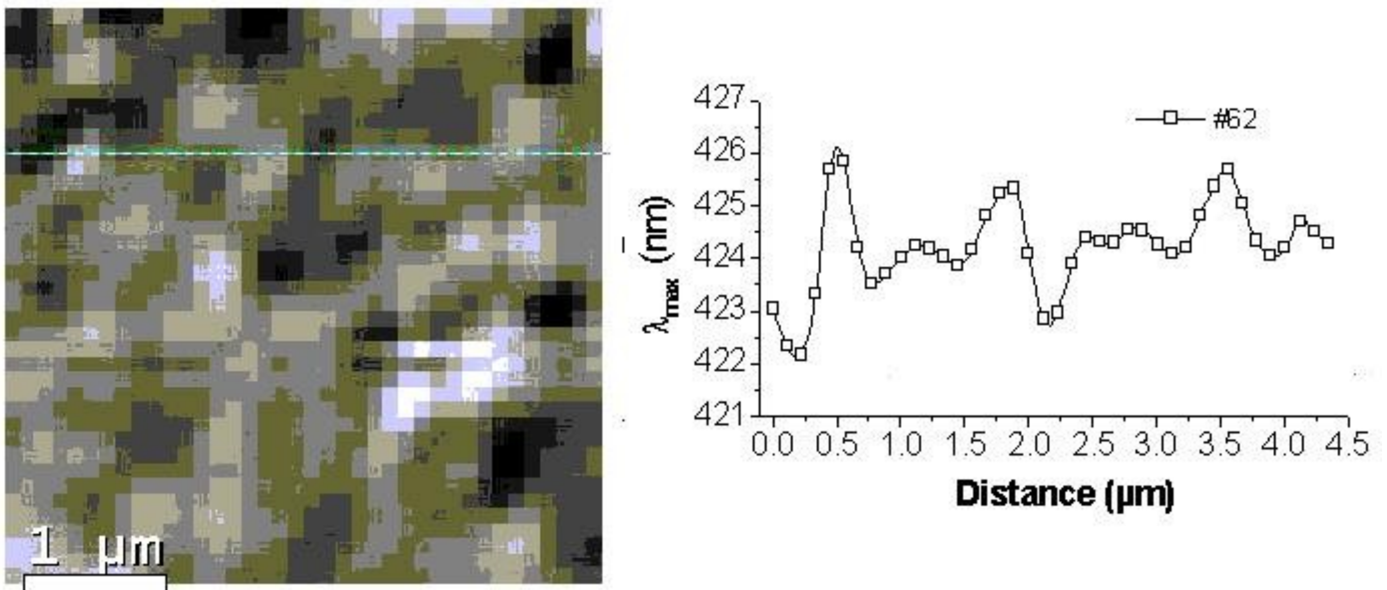

Fig. 4: Panchromatic CL image taken on sample #62 and corresponding wavelength distribution along the marked line

The homogeneity at the micro scale was studied by CL mapping. The panchromatic image, shown in Figure 4 together with the λ_{max} distribution, exhibits the granular–like contrast typical of nitride layers [2,3], i.e. grains with dimensions of less than 1 μm. From the wavelenght profile a spread of peak wavelength of +/– 2 nm is found, which can be interpreted in terms of In clustering (small incorporation fluctuations or post–growth gettering effects) in agreement with the granular structure of the map. The idea of post–growth gettering is supported by previous TEM investigations which showed in our samples an average threading dislocation density around 10^{10} cm^{-2}, with a strong tendency for the dislocations to group together in small loops of 100 – 150 nm diameter, rather than distributing randomly. Considering the fact that the CL contrast does not reflect the exact dimensions of defects but, due to carrier diffusion, it covers a broader area, the dimensions of clusters seen in CL map lead to think that the In accumulation is somewhat driven by these dislocation clusters. A further hint in this sense is provided by the intensity of the broad disorder Raman band centred at about 680 cm^{-1} which increases remarkably for increasing In molar fractions (see Figure 1).

It should also be noted that the wavelength change of +/–2nm (i.e. about +/–10 meV) over micrometric distances corresponds to variation of the In fraction of +/– 0.005. In other words, the granular structure of sample 62 (Figure 4) is produced by a $In_xGa_{1-x}N$ alloy where x changes by +/–0.005 with respect to his average value. If bunches of dislocations rather than individual dislocations really act as getters for In, it is to be expected that the In fluctuations can be minimized after a substantial reduction of the dislocation density.

The employed micro–Raman, PL and CL techniques detected a general tendency for In molar fraction to increase from the wafer center to the periphery. The slope and shape of In content are however very different in the three samples: for example the composition profile of sample 62 was quite flat up to about 13 mm from centre (see Fig. 3b) then it increased in the final 10 mm rim. On the other hand, sample 72 exhibited a nearly linear behaviour over the distance between centre and a radius of about 20 mm, where the peak wavelength passed from 415 nm to 435 nm and a steep increase occurred only at the extreme periphery where the wavelength reached 456 nm. It is difficult to give a correct interpretation of the observed profiles, because the samples 62 and 72 were grown under different conditions, such as precursor partial pressures, temperature (820 °C for sample 62 and 800 °C for sample 72), total reactor flow and substrate rotation (675 rpm for sample 62 and 200 rpm for sample 72). Moreover, the thickness of sample 72 was uniform while sample 62 was 1.5 μm in the centre and 1.41 μm at the periphery. It is strange that the layer with uniform thickness exhibits the most pronounced gradient. At the present stage of investigation we suspect that the rotation speed and the total flow in the reactor play a dominant role in the species transport and in shaping the boundary layer, which ultimately determines the different In profiles.

Conclusions

InGaN epilayers grown by MOVPE were studied by Raman spectroscopy, PL and spectrally–resolved CL. It was found that the lattice disorder increases for increasing In fractions and that In incorporation is non–uniform at the microscopic scale. The In molar fraction is seen to change by +/– 0.005 respect to the average value. Dislocations may be responsible for this clustering effect. Finally, the In molar fraction was seen to increase along the radius, between centre and periphery, probably because of the boundary layer shape imposed by reactor flowdynamic conditions.

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