

Optical and structural characterization of GaN grown by MBE using Indium as a surfactant

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Recently it has been shown that use in GaN MBE growth of surface active agents (surfactants) mediating surface reconstruction can result either in quantum dot formation, as in the case of Si [1], or in a significant improvement of optical and structural quality of epilayers, which is reached by growth under an incident In flux [2, 3]. It has been proposed that the main role played by In atoms is to modify the GaN surface kinetics [3]. The observed phenomena stimulate an enhanced interest in this mode of GaN growth, especially in the case of MBE with its possibility to operate in the very vicinity of $N/III \sim 1 : 1$ growth conditions. The surfactant mediated GaN growth is conventionally carried out at a typical temperature of 600–800°C, when the theoretically expected incorporation of In is limited by about 4% [4]. The really incorporated portion of In, estimated from the near-band-edge emission energy, is even less, being practically negligible. Due to this fact the epilayers were considered as isoelectronically doped GaN:In [2]. Note that isoelectronic doping is currently considered as a subtle instrument for controlling native point defects and electrically active impurities [5]. For this purpose, a certain critical dopant concentration should be obtained, typically in the range of $4 \times 10^{19} - 10^{20} \text{ cm}^{-3}$, resulting in overlapping the local strain fields induced by the impurities in a crystal lattice. However, until now there are no experimental data elucidating an actual In position in a crystal lattice of GaN layers grown with the additional In flux. Also a mechanism of the In influence on structural properties is not well understood.

In this paper we present the results of structural and optical studies of GaN:In, carried out to elucidate peculiarities of In incorporation in the surfactant mediated growth. The structures studied were grown by MBE on a (0001) sapphire substrates using a EP 1203 MBE setup equipped with a standard ASTEX ECR nitrogen activator. The growth was started from the sapphire nitridation stage at 1000°C during 1 hour. Then the deposition of GaN with an In flux was performed at the temperature varied in the 570–800°C range. The GaN:In was deposited immediately (for absorption measurements) or after about 200 nm thick GaN buffer layer growth.

Secondary ion mass spectroscopy (SIMS) was used for direct determination of In concentration in GaN:In epilayers. The impurity depth distribution in GaN:In and reference GaN samples was measured on a CAMECA IMS 3F instrument using O_2^+ as primary species. InN epilayers of perfect crystal quality, grown in the same MBE setup, were used for calibration of In content, whereas undoped GaN layers gave us the background In level. Figure 1 shows SIMS profiles of 1.15 μm — and 0.28 μm — thick GaN:In samples. In the thicker sample one can see a graded In concentration within the region adjacent to a 0.2 μm — thick undoped GaN buffer. In both samples there is an In increase near the

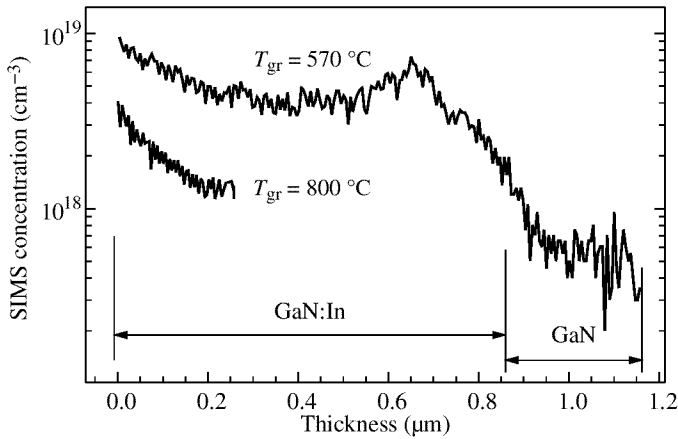


Fig. 1. SIMS profiles of In concentration in GaN:In samples grown at different temperatures.

surface, probably due to a segregation effect. However, in the volume of the thick GaN:In layer the In concentration is almost constant. In the samples studied the value varies in the range of $(1-5) \times 10^{18} \text{ cm}^{-3}$ corresponding to the In content less than 0.01%.

The In content of in $\text{In}_x\text{Ga}_{1-x}\text{N}$ may be independently estimated from x-ray diffraction (XRD) studies [6], assuming a substitutional indium incorporation into the Ga lattice sites. XRD measurements were performed using $\text{CuK}\alpha_1$ radiation in double and triple crystal x-ray diffractometers. The details of the XRD studies were described elsewhere [7]. The initial curvature of a one-side polished sapphire substrate was previously measured and taken into account. Surprisingly, the In concentration obtained from XRD data turned out to be much larger than the value given by SIMS. For example, in thick samples grown at 570°C it is about 1020 cm^{-3} ($x \sim 0.3\%$). The discrepancy between SIMS and XRD concentration of In (more than one order) causes us to conclude that under the specific growth conditions In atoms incorporate into interstitials rather than occupy the Ga lattice sites, or even form clusters at surface imperfections like grain boundaries. In this case a larger effect of In on the lattice parameters is expected, which may hardly be estimated using simple models.

To investigate the influence of In incorporation on optical characteristics, low temperature (5 K) photoluminescence (PL) measurements were performed in both the GaN:In samples and the reference $0.35 \mu\text{m}$ — thick GaN sample. In contrast to the PL spectrum of the undoped GaN, displaying a single narrow near-band-edge PL peak (Fig. 2, dotted line), an additional wide emission band appears in the GaN:In PL spectrum in the 3.35–3.45 eV range. The PL band is clearly composite and, in general, possesses a constant shape in different GaN:In samples with some variation in intensities of constituent peaks (Fig. 2, solid lines). The higher PL intensity corresponds to the higher growth temperature, although the 800°C sample is thinner ($0.28 \mu\text{m}$ instead of $1.15 \mu\text{m}$) and was grown without a buffer. Note also that the integral PL intensity in all GaN:In samples is larger than that in the undoped GaN. The band edge sharp peak I_2 (about 7 meV wide) is apparently due to neutral donor-bound exciton D^0X , while the lowest line (3.28 eV) is usually attributed to donor-acceptor pair (DAP) recombination. However, the origin of the 3.428 eV and 3.378 eV wide bands (labelled here as I_x and I_3 , respectively) is under question. The intensity of the I_x and I_3 lines drops faster than I_2 with a temperature increase, especially of I_x . The insert in Fig. 2 presents the temperature dependence of the integrated PL intensity

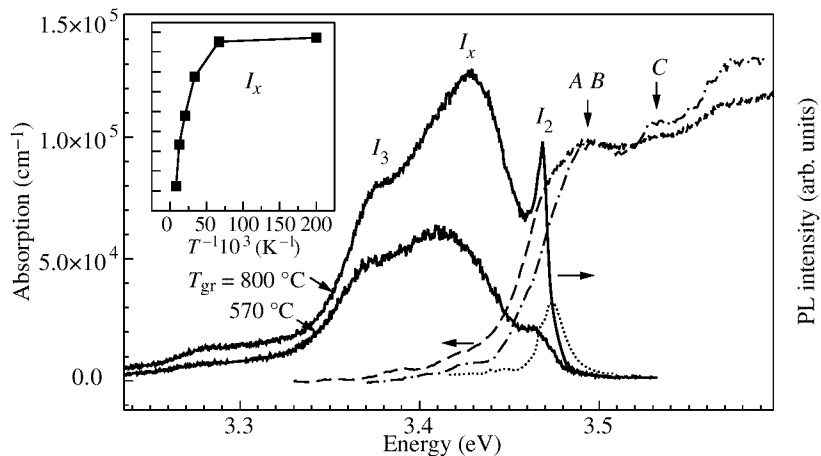


Fig. 2. Low temperature (5 K) PL spectra measured in GaN:In samples (solid curves) grown at different temperatures and in a reference GaN sample (dotted curve). Absorption spectra are shown for a GaN:In sample (dashed curve) and an undoped GaN (dash-dotted curve). The integrated intensity of the I_x peak versus reciprocal temperature is presented in the inset.

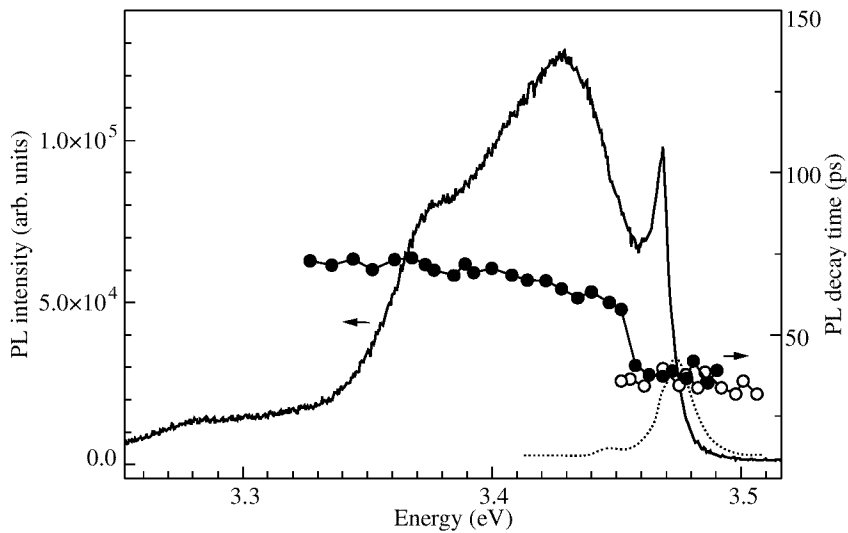


Fig. 3. Decay times of PL in undoped GaN (open circles) and GaN:In (solid circles) samples. Cw PL spectra are presented for GaN:In (solid line) and GaN (dotted line).

of the I_x peak, giving a thermal activation energy E_A of 11.8 meV. The main characteristic of the I_3 line is a well-resolved blue shift (about 6 meV in the temperature range from 5 to 50 K), which is typical for PL of thermally-occupied localized states.

To clarify the origin of the complicated PL band, transmission spectra were measured in the $0.28\ \mu\text{m}$ — GaN:In and $0.35\ \mu\text{m}$ — GaN samples, grown without buffer layer. The peculiarities corresponding to unresolved A and B excitons and a separated C exciton are obviously pronounced and are similar in both samples. However, a smooth shoulder below A–B exciton peak is registered in the GaN:In sample, evidencing an additional

inhomogeneously broadened absorption edge, shifted to about 20 meV below the A exciton. Assuming formation of $\text{In}_x\text{Ga}_{1-x}\text{N}$, it corresponds to $x = 1.3\%$ that is even higher than the value obtained from XRD. To explain this fact, one can suggest formation of $\text{In}_x\text{Ga}_{1-x}\text{N}$ clusters. Since the hypothetical $\text{In}_x\text{Ga}_{1-x}\text{N}$ and GaN edges coexist in the spectrum, the states forming the absorption edges should be spatially separated.

Time-resolved (TR) PL measurements also confirm the composite character of the PL band in GaN:In. The decay time within the PL contour is not monoexponential. In particular, there is a noticeable contribution of long-living PL (the signal is not vanishing in the 12 ns between the exciting laser pulses). However, the first one-two orders of the PL decay take place in first 100–200 ps with the characteristic decay times plotted in Fig. 3 as diamonds. The time for the low-energy band smoothly depends on the wavelength, increasing to the red side. Accounting for the broadening of the absorption band edge, one possible explanation of this relatively fast contribution to the PL signal may be recombination at the tail localized states, somehow related to the In-rich clusters. Note, that the narrow peak visible in both GaN and GaN:In samples exhibits decay times in the range of 30–50 ps, which is well consistent with the data for D^0X [8].

In conclusion, the structural and optical characterisation of GaN:In epilayers have shown that only a small amount of In is incorporated into the Ga sites, making the layers to be considered as not pure “isoelectronically” doped. The In atoms presumably occupy interstitial positions in the crystal lattice, concentrate on mosaic grain boundaries and have a tendency to form clusters. The In nucleation near structural defects, like e.g. nano-pits, may recover the lattice structure, increasing the integral PL intensity. Besides, like at conventional isoelectronic doping, local strains induced by the inhomogeneous In distribution may activate mechanisms of structure improvement. On the other hand, the possible occupation of interstitials by the In atoms can hardly be considered as a positive factor.

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