Investigation of Statistical Broadening in InGaN Alloys

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Abstract. Optical and structural properties of thick InGaN layers grown by MOCVD and MBE were studied by photoluminescence, optical transmission and Raman spectroscopies and X-ray diffraction analysis. Optical bandgap, Urbach energy, and full widths at half maximum (FWHM) of photoluminescence and Raman spectra depending on the InGaN alloy composition were determined experimentally. Minimal theoretical linewidth of photoluminescence spectra resulted from random distribution of In and Ga atoms in cation sublattice was calculated.

1. Introduction

Indium gallium nitride (InGaN) is successfully used as active region of light-emitting and laser diodes based on III-nitrides. In contrast to GaN whose electronic properties are the most accurate estimated among binary III-nitrides, the value of InN bandgap has been a contentious issue for a long time. The early experiments have given the overestimated bandgap value of 1.5-2 eV [1] due to insufficient crystal quality of the InN layers. More recent studies of better-quality single-crystalline epilayers have provided strong evidences that the bandgap of InN is close to 0.7 eV [2].

Investigation of InGaN ternary alloy material is of great interest since difference between bandgaps of its binary components is very large (E_{g InN}~0.7 eV, E_{g GaN}~3.4 eV). Theoretically, the use of InGaN as active region enables fabrication of optoelectronic devices, operating in the entire visible, near-UV and near-IR ranges of spectrum (figure 1). The composition dependence of InGaN bandgap is nonlinear with downward bowing behaviour. There is still uncertainty about the value of the bowing parameter, the values in the range from 1 eV to 4 eV have been reported; composition-dependent bowing parameter also has been suggested.

As one can see in figure 1, lattice constants of InN and GaN differ considerably. The mismatch results in a tendency to clustering and phase separation in ternary alloy. Localization of excitons in the clusters takes place significantly affecting optical properties of InGaN layer [3]. Theoretical calculation shows that there could be a miscibility gap in free-standing layers as well as in biaxially strained ones. In the latter case, the gap is shifted towards higher indium concentration area [4]. However, despite of some experimental evidence, the actual existence of the miscibility gap is questionable. Further details on other InGaN properties can be found elsewhere [1, 5].
2. Alloy broadening in InGaN

Since InGaN is a ternary alloy, consisting of two group-III elements (In and Ga), there is some distribution of the atoms in the cation sublattice, which cannot be found in elemental group-IV and binary III-V or II-VI semiconductors. Experimental values of the full width at half maximum (FWHM) of the photoluminescence (PL) spectra of ternary alloys are higher than expected from the thermal broadening only (especially at low temperatures). Under the assumption that In and Ga atoms are distributed randomly in the sublattice and without taking into account other broadening mechanisms (e.g. inferior crystal quality, defects, alloy clustering, etc.), the minimal theoretical FWHM of PL spectra can be calculated using equation (1) in accordance with [6]:

$$\text{FWHM} = 2.36\sigma_B = 2.36 \frac{dE_g}{dx} \left(1 - x\right)^{1/2}$$

(1)

where $E_g$ is composition dependent bandgap of In$_x$Ga$_{1-x}$N, $K$ is cation concentration and $V_{exc}$ is excitonic volume. Note that in contrast to zincblende AlGaAs with the almost invariable lattice constant in the whole composition range, InGaN is a wurtzite semiconductor with significantly different lattice constants of its binaries, therefore the cation concentration is given as

$$K = 4/\left(\sqrt{3}a^2c\right)$$

(2)

where $a$ and $c$ – composition dependent in- and out-of-plane lattice constants, respectively. Calculated FWHM is plotted in figure 2.

3. Samples and experimental details

Two sets of samples were grown on sapphire (0001) substrates with GaN buffer layer. The low and moderate In content sample were grown by metalorganic chemical vapor deposition (MOCVD); trimethylgallium and trimethylindium were used as the group-III source materials; ammonia was used as the nitrogen source. The set of In-rich samples was grown by molecular beam epitaxy. The thickness of InGaN layers was estimated as 0.5 um; the layers are considered to be fully relaxed and undoped.

X-ray diffraction analysis under the assumption of the Vegard’s law was performed using D8 Discover Bruker diffractometer in order to determine the indium content of the samples. Room and liquid nitrogen temperature photoluminescence studies were carried out using excitation of He-Cd (325 nm) and YAG:Nd (532 nm) lasers depending on In content. Room temperature optical transmittance measurements were performed with halogen lamp as a light source. Raman spectra were measured at room temperature on a Horiba Jobin-Yvon T64000 triple spectrometer, equipped with a confocal microscope, which allows obtaining information from the area of about 1 um. All spectra
were recorded in \(z(\mathbf{x})\bar{z}\) backscattering configuration with the \(z\) direction oriented along the \(c\)-axis of the sample. Only \(A_1(LO)\) and \(E_2\) (high) optical phonon modes are allowed in this configuration.

4. Results.
Normalized PL spectra at 77 K are shown in figure 3. It is clearly visible that the spectra of binaries (\(\text{InN} - 1\) and \(\text{GaN} - 14\)) are much narrower than the spectra of their ternary alloys. The dependence of the optical bandgap at 300 K, obtained by Tauc method [7], on the indium content is shown in figure 4. The best fit is achieved with bowing parameter \(b=2.15\) eV, which is in good agreement with literature values.

![Figure 3. Normalized PL spectra of \(\text{In}_{x}\text{Ga}_{1-x}\text{N}\) alloys at 77K with (1) \(x=1\); (2) \(x=0.95\); (3) \(x=0.89\); (4) \(x=0.67\); (5) \(x=0.50\); (6) \(x=0.40\); (7) \(x=0.34\); (8) \(x=0.21\); (9) \(x=0.17\); (10) \(x=0.13\); (11) \(x=0.10\); (12) \(x=0.035\); (13) \(x=0.02\); (14) \(x=0\).

Figure 4. Optical bandgap of \(\text{In}_{x}\text{Ga}_{1-x}\text{N}\) alloy at 300 K.

The absorption edge of semiconductors is not abrupt and an exponential part called Urbach tail exists below the optical bandgap (figure 5). The origin of the tail can be related to statistical broadening, but it is not well understood yet. The spectral dependence of the absorption coefficient below the bandgap is described by empirical rule:

\[
\alpha(h\nu) = \alpha_0 \exp \left( \frac{h\nu}{E_U} \right)
\]

where \(\alpha_0\) is a constant and \(E_U\) is a characteristic Urbach energy. The reciprocal of the slope of the straight-line segment of the \(\ln(\alpha)\) versus \(h\nu\) curve is the value of the Urbach energy (figure 6).

![Figure 5. Tauc plot for the sample with \(x=0.05\).

Figure 6. Urbach energy estimation for the sample with \(x=0.05\).
The values of PL FWHM at 77 K and 300 K and Urbach energy as a function of alloy composition are shown in figure 7 (a), (b) and (c), respectively. As one can see, the experimental points follow the shape of the theoretical curve, but the values are three or four times greater than the theoretical ones. The discrepancy may provide some evidence for the not truly random distribution of the In and Ga atoms [8] or existence of other broadening mechanisms in addition to the thermal and alloy ones. Also, there are some outliers in the composition range of ~40-60% (circled in red in the figures), which may be related with the miscibility gap or very poor crystal quality of the layers.

The experimental and calculated (in accordance with [9]) FWHM of Raman spectra for the A_1(LO) and E_2(high) modes are shown in figure 8. It is clear that composition dependency is asymmetric with respect to $x=0.5$ as well as PL FWHM and Urbach energy curves, but the maximum of the A_1(LO) curve is shifted to compositions near the low bandgap semiconductor (InN) unlike the E_2 (high) curve (see part 6.8 in [5]). Moreover, the outliers exist near $x=0.5$, similar to PL FWHM and Urbach energy data, which may also favour miscibility gap or very poor crystal quality.

5. Conclusions.
The composition dependence of linewidths of photoluminescence and Raman spectra of thick In$_x$Ga$_{1-x}$N layers in the entire composition range was investigated. Optical bandgap dependence on the alloy composition was obtained by Tauc method. The experimental values of the PL FWHM are much greater than theoretical FWHM resulted from random distribution of In and Ga atoms in cation sublattice (alloy broadening), suggesting that distribution of group-III atoms is not truly random and/or
other broadening mechanisms take place. The outlier points on the graphs indicate that epitaxial growth of high-quality single-crystal In_{x}Ga_{1-x}N layers in the composition range 0.4<x<0.6 is currently challenging. It can be related either to inadequacy of current epitaxial technology or to fundamental physical limitations due to miscibility gap.

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