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Local strain distribution of hexagonal GaN pyramids

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Abstract

Self-organized hexagonal GaN pyramids of 5 μm width and covered by six {1 1̲ 0 1} side facets were investigated by spatially resolved cathodoluminescence and micro-Raman spectroscopy. Beside a narrow luminescence peak at 355 nm, originating from the 2 μm thick GaN layer, an additional broad luminescence band was observed from the GaN pyramids around a wavelength of 357 nm. A strong energy shift is found along the {1 $\bar{1}$ 0 1} pyramidal facets and directly visualized by monochromatic CL images and linescans. The effect of the thermal strain due to the mismatch of the thermal expansion coefficient of the various layers involved was analyzed by micro-Raman spectroscopy and by varying the temperature from 5 K to room temperature. A strong impact of the free-carrier concentration on the local band gap and its temperature dependence was found. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Wide-band-gap group-III nitrides are being studied extensively for their application potential in optoelectronic and microelectronic devices. Selective growth techniques will play a key role in this field along with the control of strain in low-dimensional heterostructures based on GaN. In order to fabricate micro- and nanostructures, dry etching is usually employed often resulting in severe damage and contamination of the surface. Selective epitaxial growth, which has been proven to enable three-dimensional control of microstructures as quantum wires and quantum dots in ordinary III–V-compounds, overcomes those problems. Using metal organic vapor-phase epitaxy (MOVPE), selective growth of GaN and AlGaN on linearly patterned GaN(0 0 0 1)/sapphire substrate was reported [1] and three-dimensionally controlled structures were reported recently [2,3]. Due to the large mismatch of lattice constant and thermal expansion coefficient between GaN

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and the sapphire substrate, the patterned pyramidal geometry results in a strongly inhomogeneous three-dimensional strain distribution as well as strongly inhomogeneous dislocation density and impurity incorporation. It is the purpose of this paper to optically characterize these self-organized GaN pyramids on a microscopic scale.

2. Experimental procedure

The selective epitaxial growth of GaN was performed on a 2 μm thick GaN (0 0 0 1) layer grown on a sapphire (on axis α-Al_2O_3 $(1\,1\,\underline{2}\,0)$) substrate using an AlN buffer layer. A 50–60 nm thick SiO_2 mask was patterned by photolithography and subsequent etching to form hexagonal windows. The pattern consists of three periodic triangular lattices of hexagons having a width of 5 μm and lateral distances of 10, 20, and 40 μm, respectively. Finally, GaN was selectively grown on the top, creating the periodic arrays of hexagonal shaped pyramids covered by the six $\{1\,\underline{1}\,0\,1\}$ pyramidal facets. No GaN is deposited on the SiO_2 mask. Growth details are given elsewhere [2,3].

The microscopical optical characterization was performed using spatially resolved cathodoluminescence (CL) and micro Raman spectroscopy. While the exciting focused electron beam of a modified scanning electron microscope (SEM) is digitally scanned over the sample area under investigation, a complete CL spectrum is recorded and stored at every pixel position. The complex and massive data set of spatially and spectrally resolved CL, i.e. $I(x, y, \lambda)$, is then evaluated to obtain local CL spectra $I(x_i, y_i, \lambda)$ and CL linescans $I(s, \lambda)$. All spectra and linescans are recorded simultaneously together with the standard SEM picture within one single scan of the e-beam. Details of the different modes of CL microscopy and the performance of the setup are given elsewhere [4]. Micro-Raman measurements were carried out with a triple-grating Dilor spectrometer and the 514.4 nm line of an Ar^+ laser for excitation. The spatial resolution was better than 1 μm. We were able to detect Raman shifts smaller than 0.1 cm^{-1}.

3. Results and discussion

The spatially integrated low temperature (5 K) CL spectrum is shown in Fig. 1, together with local CL spectra obtained from the flat 2 μm GaN layer between the masked pyramids as well as the spectrum originating from the pyramids, respectively. Besides a narrow luminescence peak at $\lambda_1 =$ 355.0 nm ($E_1 = 3.492$ eV) with a FWHM = 8 meV, stemming from the 2 μm thick GaN layer below the SiO_2 mask, an additional broad luminescence band is observed as a weak shoulder in the integral spectrum and is identified in the local CL as originating from the pyramids. This band is centered around $\lambda_p = 357.1$ nm (i.e. $E_p = 3.471$ eV) and is very broad with a FWHM = 52 meV, which indicates local band gap fluctuation within the pyramid. This band-gap gradient from the base to the top of the GaN pyramids can be directly visualized through monochromatic CL images. Starting with an emission wavelength of 355.6 nm at the very top and at the edges of the pyramid, the whole upper 80% of the pyramid shows bright CL when λ is approaching 357.1 nm (3.471 eV), i.e. the emission

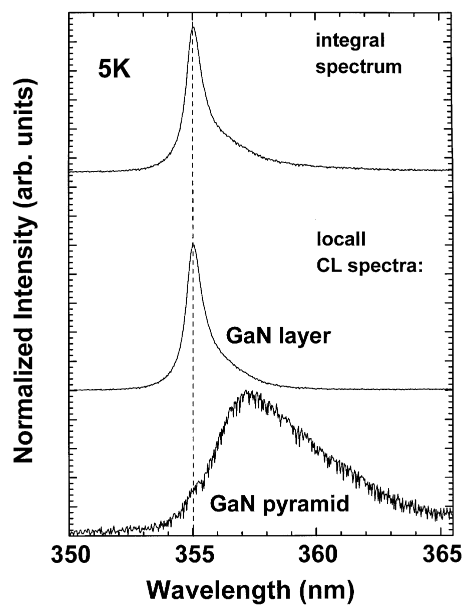

Fig. 1. Local spot-mode CL spectra taken at positions on the GaN pyramid and in between pyramids, compared with a spatially integrated CL spectrum.

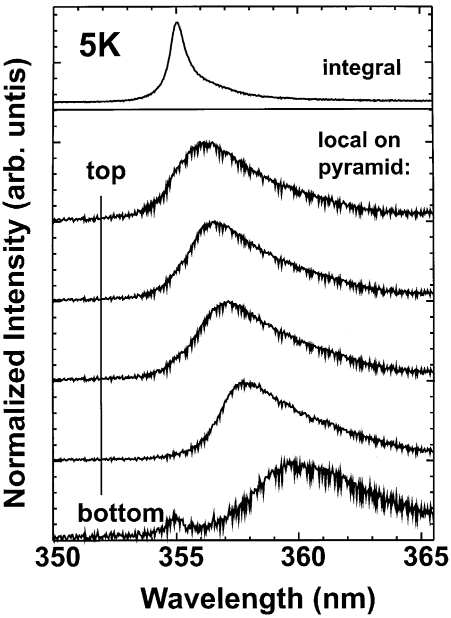

Fig. 2. Set of monochromatic CL images recorded at $T = 5$ K.

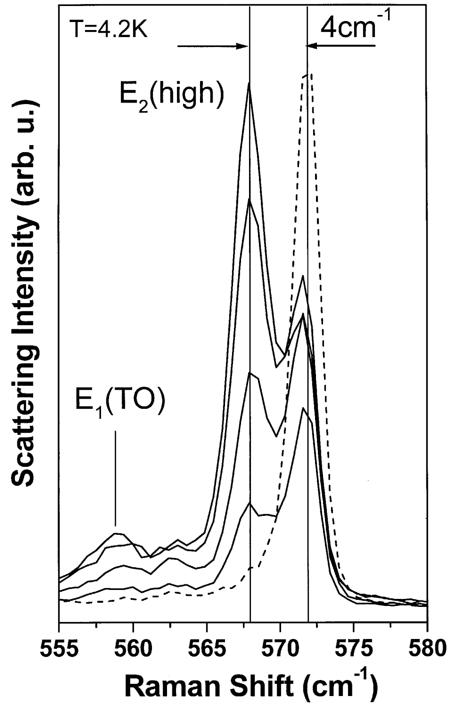

Fig. 3. Raman depth profile at $T = 4.2$ K. The solid curves represent spectra taken from various depths of the pyramid, the spectra from the 2 μm GaN epilayer is shown as dashed curve.

of (D^0, X) for unstrained or completely strain-relaxed GaN [5]. In addition, a strongly red-shifted CL with $\lambda > 360.6$ nm is emitted from the base area of the pyramid. A set of local CL spectra recorded at different positions along a $\{1\,\underline{1}\,0\,1\}$ facet from the bottom to the top of a pyramid which is plotted in Fig. 2 strongly confirms this observation. The different emission energies reveal the compressive strain of the 2 μm thick GaN layer in contrast to the gradual relaxation of strain along the pyramid. From micro-Raman measurements performed spatially resolved at a position between the pyramids as well as focused on top of the pyramids, a compressive biaxial stress of $\sigma_a = 0.95$ GPa (taking into account the best know value of $4.2 \pm 0.3\ \mathrm{cm}^{-1}$ GPa^{-1} for the E_2(high) Raman mode [6]) was found for the 2 μm GaN layer whereas no stress is found when averaging over the pyramids see Fig. 3. Thus, the CL results are in perfect quantitative agreement with the strain distribution obtained from Raman microscopy.

This is even more pronounced in the CL linescan along a pyramid edge, displayed in Fig. 4. The scan is indicated by a white line in the SEM picture in the inset of Fig. 4. The position $s = 0$ μm indicates the base of the GaN pyramid, where a strongly red-shifted luminescence ($\lambda > 361$ nm, i.e. $E < 3.433$ eV) is observed. During the lower first 3 of the 10 μm distance along the pyramid's edge, a blue shift up to $\lambda \leqslant 357.2$ nm, which equals (D^0, X)-emission of totally strain-relaxed GaN occurs. Obviously, the upper $\frac{2}{3}$ of the pyramid volume is strain-free, in perfect agreement with the results from Raman microscopy.

To understand the impact of thermal strain due to the mismatch of thermal expansion coefficients, CL spectral images were measured not only at He temperature but up to $T = 300$ K. The spectral peak position of the CL integrated over the non-pyramid area of the GaN layer and the peak energies of the CL spectra integrated over the whole GaN pyramid was investigated as a function of sample temperature. It was found that the GaN layer luminescence is in good agreement with the theoretical $E_{(D^0,X)}(T)$-dependence for unstrained

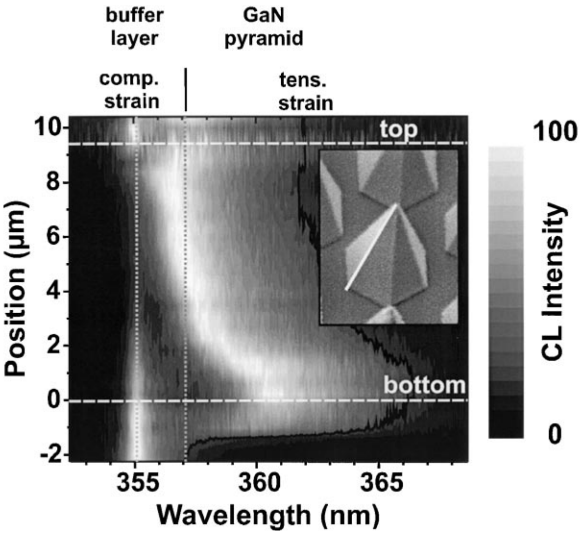

Fig. 4. CL spectrum linescan $I(\lambda, s)$ at $T = 5$ K along the edge of a GaN pyramid, indicated as white lines in the SEM-picture (inset). The dashed white lines mark the bottom and top position of the GaN pyramid. The spectral position of (D^0, X)-emission from the compressively strained 2 μm GaN layer (355 nm) as well as from the completely relaxed GaN (357.1 nm) are marked by doted lines.

GaN, following Varshni's rule:

$$E_{(D^0,X)}(T) = 3.471\ \text{eV} - 5.08 \times 10^{-4}\ \text{eV/K} \cdot T^2/(996\ \text{K} - T) \quad (1)$$

(parameters taken from Refs. [3,7]), taking into account a compressive stress of 0.95 GPa at 2 K, which decreases by $\frac{1}{3}$ when reaching 300 K. However, the luminescence recorded from the GaN pyramids completely contradicts this rule. The strong red-shift becomes even more pronounced with increasing temperature, reaching $\Delta E < -50$ meV at 150 K. This shift cannot be caused solely by strain effects. The influence of the free-electron concentration on band gap via the Burstein–Moss-shift and the band-gap renormalization on the $E_g(T)$-dependence in GaN was discussed in Refs. [5,8]. Incorporation of oxygen stemming from the SiO_2 mask, which is a well known donor in GaN, within the firstly grown GaN layers at the base of the pyramids might easily be responsible for a free-electron concentration $n > 10^{20}\ \text{cm}^{-3}$ and could strongly influence the local GaN band gap and its temperature dependence.

4. Conclusions

In conclusion, we visualized directly the local band-gap modulation in self-assembled selectively grown hexagonal GaN pyramids by cathodoluminescence microscopy. Locally varying strain and strain relaxation is investigated and quantitatively correlated with the results from Raman spectroscopy. While the results obtained for the 2 μm thick GaN layer may be understood completely in terms of a compressive biaxial stress of 0.95 GPa (at 2 K) which is partially relieved with increasing temperature, the luminescence recorded along the GaN pyramids shows strong indication of local incorporation of impurities (oxygen) at the bottom of the pyramids. All strain is completely relaxed in the upper part of the GaN pyramids.

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