Vertical strain and doping gradients in thick GaN layers

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We report on spatially-resolved low-temperature luminescence and Raman experiments on a 220-μm-thick GaN layer grown on sapphire by hydride vapor phase epitaxy. Our measurements reveal that the peak position of the near-band-gap luminescence strongly depends on the distance to the substrate interface. The luminescence shifts continuously to lower energies with decreasing distance but a strong blue shift occurs directly at the interface. We correlate these effects with the inhomogeneous free-carrier distribution and the strain gradient found by our Raman experiments. © *1997 American Institute of Physics.* [S0003-6951(97)02343-7]

A major problem in growing GaN epitaxially is the large mismatch of lattice constants and thermal expansion coefficients between layer and common substrates, e.g., sapphire or GaAs.[1] Consequently, most GaN layers and also their substrates are highly strained. The unfavorable growth conditions result in high defect concentrations in the layers which are not homogeneously distributed.[2,3] To study the spatial varying (in particular, the thickness-dependent) influence of strain and defects on the optical properties in heteroepitaxial GaN, we performed spatially-resolved cathodoluminescence (CL) experiments on a thick GaN layer deposited on sapphire. This technique allowed us to map the vertical luminescence distribution in the layer, thus extracting the dependence of the optical properties on layer thickness. In order to obtain independent information about the strain and the doping distribution in the layer, we carried out micro-Raman scattering experiments of the same region investigated by CL measurements. This enabled us to correlate structural with optical properties of regions as small as 1 μm. In contrast to an investigation on a series of samples with varying thicknesses, spatially-resolved measurements avoid possible mistakes caused by comparing different samples grown and treated under slightly different conditions.

The sample under study was an undoped, 220-μm-thick hexagonal GaN layer grown on (0001) sapphire using hydride vapor phase epitaxy with a ZnO buffer layer. Details of the growth method may be found in Ref. 4.

Low-temperature CL measurements were performed in a fully computer-controlled modified scanning electron microscope with a spatial resolution of about 100 nm. Details are given in Ref. 5.

Micro-Raman measurements were carried out with a triple-grating Dilor spectrometer and the 515.4 nm line of an Ar^+ laser for excitation. The lateral spatial resolution was better than 1 μm. The microscope and confocal optics restrict the focal depth to 2 μm. We were able to detect Raman shifts smaller than 0.1 cm^{-1}.

Our measurements reveal that the energy positions of the excitonic luminescence change drastically when moving the exciting electron beam from the surface of the GaN layer nearer to the substrate interface, as can be seen from the CL linescan displayed in Fig. 1. The luminescence is dominated by the free-exciton emission (FX) and the neutral-donor-bound exciton emission (I_2), which peak at 356.5 nm (3.478 eV) and 357.1 nm (3.472 eV), respectively, when exciting the layer near the surface. Because of the elevated temperature of 25 K, the I_2 and the free-exciton emission appear in equal intensity. Starting from the surface of the layer (distance $d = 220$ μm) and proceeding in direction of the substrate interface ($d = 0$ μm), one can see that the peak positions of the excitonic luminescence remain nearly constant during the first 50 μm. In contrast, from $d \approx 170$ μm to $d \approx 35$ μm the spectra exhibit a continuous red shift of about 6 meV in total. Proceeding further towards the substrate interface the red shift gives way to a significant blue shift and the luminescence peaks become broader. Directly at the interface the maximum intensity of the luminescence is found at 352.7 nm (3.515 eV).

It is important to note that the red shift of the excitonic

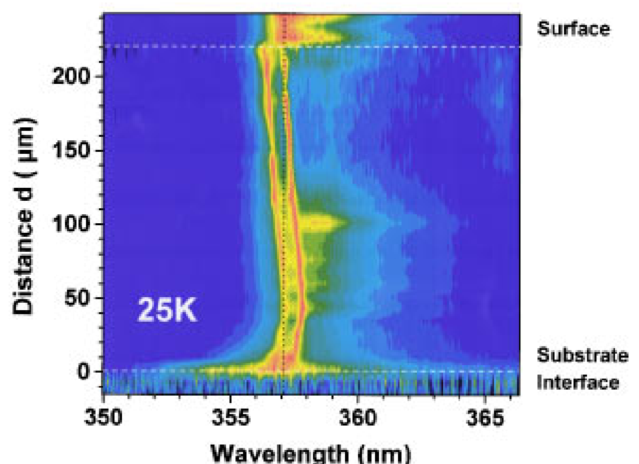

FIG. 1. CL linescan along the GaN cross section taken at 25 K. Red color indicates high luminescence intensity, blue color low intensity.

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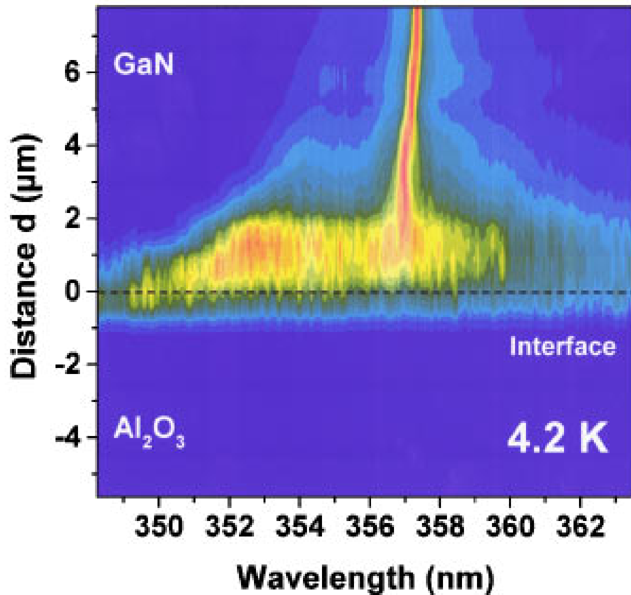

FIG. 2. High-resolution CL linescan taken directly at the substrate interface at 4.2 K.

luminescence was observed both for the I_2 and for the free-exciton emission. Consequently, a different excitonic recombination process such as, e.g., excitons bound to a different donor, can be ruled out as an explanation for the red shift.

From the high-resolution CL linescan in Fig. 2, which displays the luminescence distribution directly at the substrate, it becomes clear that two different types of blue shifts occur near the substrate interface. The first one shifts the excitonic luminescence to higher energies and compensates the former red shift. The second one is an additional luminescence process. For distances $d<10$ μm a shoulder appears above the free-exciton emission line which increases in intensity for decreasing distance to the substrate. For distances below 2.0 μm this structure peaking at about 3.515 eV becomes the dominant luminescence process.

In order to understand the spatial dependence of the luminescence, we performed micro-Raman measurements on the same region where we took the CL linescans. All Raman measurements were carried out at low temperatures to ensure comparable conditions. By measuring the shift of the E_2 Raman mode of the GaN layer we could determine the strain in our sample as a function of the distance to the substrate (see Fig. 3). We found that the strain in the GaN layer decreases nearly exponentially with increasing distance to the substrate. The layer is already relaxed to a large extent at a distance $d\approx 35$ μm away from the substrate. For distances $d>100$ μm the layer is fully relaxed.

Figure 4 shows unpolarized, low-temperature micro-Raman spectra taken at various distances to the substrate interface taken in $x(..)\bar{x}$ scattering geometry. Near the surface of the layer only the expected GaN Raman modes peaking at about 533 cm^{-1} [A_1(TO)], 560 cm^{-1} [E_1(TO)], 567 cm^{-1} (E_2), and 742 cm^{-1} [E_1(LO), Fröhlich allowed] are present in the spectra.[6] At a distance of 160 μm, a broader structure below the A_1(TO) [the LO phonon-plasmon mode (LPP$^-$)] becomes visible. This mode shifts continuously to higher frequency with decreasing distance to

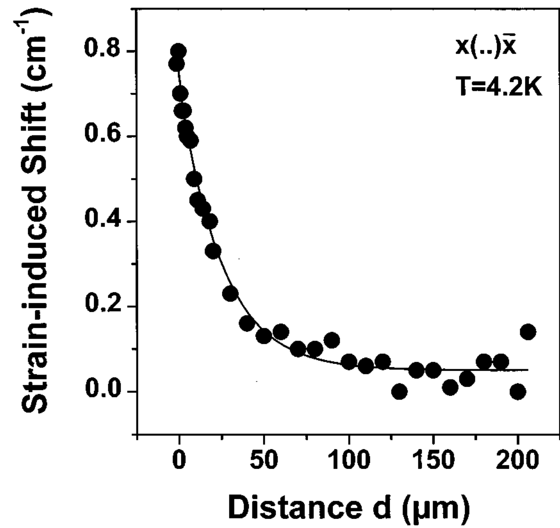

FIG. 3. Strain-induced shift of the E_2 Raman mode as a function of distance d to the substrate interface. The data were taken at $T=4.2$ K. The solid line represents an exponential fit to the data points.

the substrate. Simultaneously, an additional structure at about 650 cm^{-1} known from highly doped GaN[7,8] appears and becomes stronger for decreasing distance while the E_1(LO) decreases in intensity. This observation indicates that the free-carrier concentration in the thick GaN layer increases gradually with decreasing distance to the substrate. From the energy position of the LPP$^-$ mode we were able to estimate the free-carrier concentration. We found that the free-carrier concentration increases from about 5×10^{17} cm^{-3} near the surface of the GaN layer to 1×10^{20} cm^{-3} at the substrate interface. Thus, apart from the strain gradient, there is also a significant gradient of the free-carrier concentration in the GaN layer.

We divide our layer into four regions according to the various luminescence shifts. In the first region (220 μm$<d$

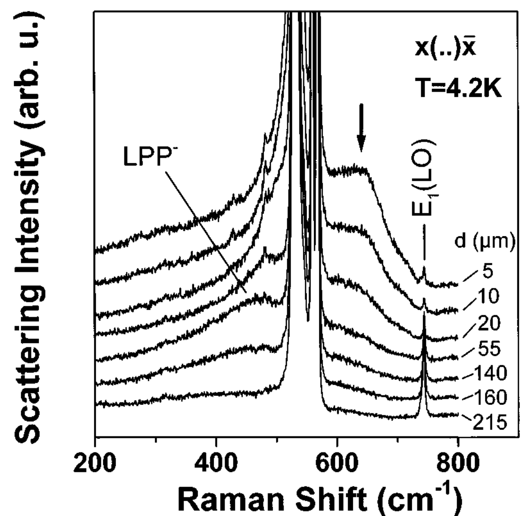

FIG. 4. Low-temperature Raman spectra taken at various distances d to the substrate interface. At 160 μm away from the substrate the LPP$^-$ mode appears and shifts to higher frequency with decreasing distance. Simultaneously a new feature known from highly doped GaN samples appears with increasing intensity (marked by an arrow).

$<170\ \mu$m) no shift can be observed; all spectra are quite similar. In the second region ($170\ \mu\text{m}<d<35\ \mu$m) the I_2 as well as the free-exciton emission shifts approximately parallel by 6 meV towards lower energy. This red shift is compensated by the following blue shift in the third region ($35\ \mu\text{m}<d<2\ \mu$m). In the fourth region a broad additional peak on the high-energy side of the free-exciton emission line becomes dominating in the spectra.

While the optical and structural properties of the first region of the GaN layer do not change remarkably with the distance to the substrate, the red shift occurring in the second region indicates a reduction of the bandgap of the GaN layer. Because this red shift can be observed for the bound- as well as for the free-exciton emission, we can rule out a different recombination channel gradually opening with decreasing distance to the substrate, e.g., a deeper-bound exciton: the binding energy remains constant over the distance. Tensile strain can also be excluded because a stress-induced shift of the excitonic PL should be accompanied by a softening of the E_2 Raman mode. Biaxial stress of one GPa shifts the near-band-edge luminescence lines by 27 meV and the E_2 Raman mode by $4.2\ \text{cm}^{-1}$.[9] From this one expects a softening of the E_2 mode by about $0.9\ \text{cm}^{-1}$, which we did not observe in our micro-Raman measurements. Instead, we found a biaxial compressive strain which decreases exponentially with increasing distance. In the region where the red shift occurs, most of the strain is already relaxed. A likely explanation for the red shift of the excitonic luminescence can be given in terms of the inhomogeneous free-carrier distribution in the layer. Our micro-Raman measurements reveal that the free-carrier concentration increases monotonously from some 10^{18} to $10^{19}\ \text{cm}^{-3}$. Consequently, bandgap renormalization induced by the free carriers leads to a gradual decrease of the bandgap.

In the third region the red shift of the excitonic luminescence turns into a blue shift. This compensates the former red shift and can simply be explained by the increasing compressive strain with decreasing distance to the substrate. The total blue shift in this region is about 6 meV. The hardening of the E_2 mode found in our micro-Raman measurements is $0.8\ \text{cm}^{-1}$, which corresponds to a change of the excitonic energy position of 5.2 meV following the relation given in Ref. 9. This value agrees very well with our finding.

Apart from the blue shift of the excitonic luminescence an additional band appears in the fourth region directly at the substrate interface. We attribute this structure, which peaks above the bandgap energy of the GaN layer, to band-to-band transitions. Our Raman experiments show that the free-carrier concentration in this region is in the range of $1\times10^{20}\ \text{cm}^{-3}$. At such a high doping density the excitons become screened, as can be seen first in a broadening and finally in the disappearance of the bound-exciton line 2 μm away from the substrate interface, and band-to-band transitions occur. Band filling leads to luminescence above the bandgap energy of GaN. Simultaneously, the built-in impurities form tail states below the conduction band which broaden the luminescence to the low-energy side.[10] Similar spectra were observed in highly doped GaN samples.[11]

The observed doping gradient has two causes. On the one hand, the defect density due to the unfavorable growth conditions decreases strongly with increasing layer thickness. The improving layer quality should consequently lower the background doping level. On the other hand, the concentration of impurity atoms diffused from the buffer layer and from the substrate into the layer during growth also decreases with increasing distance to the substrate.

In conclusion, we showed that the optical properties of heteroepitaxial GaN strongly depend on the distance to the substrate interface. We explain the observed shifts in CL and Raman by the influence of both a vertical strain gradient and an increase in free-carrier concentration with decreasing distance to the substrate.

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