DEPTH-PROFILE OF THE EXCITONIC LUMINESCENCE IN GALLIUM-NITRIDE LAYERS

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ABSTRACT

We present results of spatially-resolved photoluminescence and Raman measurements on a 200 µm thick GaN layer grown on sapphire by hydride vapor phase epitaxy. Our micro-photoluminescence measurements reveal that the peak position of the excitonic and donor-acceptor-pair transitions strongly depends on the distance to the substrate interface. We observed a strong blue shift near the interface and discuss the influence of strain, which we quantified by micro-Raman experiments.

INTRODUCTION

A major problem in growing GaN epitaxially is the large mismatch of lattice constants and thermal expansion coefficients between layer and common substrates as e.g. sapphire or GaAs [1]. Consequently most GaN epilayers are highly strained. Another problem is the inhomogeneous distribution of the photoluminescence in these layers [2,3]. In order to handle thin-film heterostructures and devices based on GaN a knowledge about the influence of strain on the optical properties as well as a control of the homogeneity is necessary.

We performed spatially-resolved photoluminescence measurements at low temperatures on GaN grown on sapphire in order to map the luminescence distribution in the layer on a micrometer scale. Micro-Raman-scattering of the E_2-mode of hexagonal GaN in the same layer regions provides us with independent information about the internal stress in the layer and allows us to correlate structural and optical properties [4].

After presenting the experimental details we first discuss the main features of the near-bandgap luminescence of the layer. We then describe the results of our spatially-resolved measurements and discuss the observations.

EXPERIMENT

The sample under study was an undoped 200 µm thick hexagonal GaN layer grown on [0001] sapphire using hydride vapor phase epitaxy (HVPE) with a free carrier concentration below $1 \cdot 10^{17}$ cm^{-3} as determined by room-temperature Hall measurements.

Micro-photoluminescence measurements were performed using a single-grating Renishaw spectrometer equipped with an UV notch filter and an UV-enhanced CCD detector. The sample was excited parallel to the substrate surface using the 325 nm line of a He-Cd laser. By passing the laser through a microscope objectice (x40, x27) the laser beam was focused to a point spot with a diameter of about 2 µm. With this micro-photoluminescence setup we reached a spatial resolution of about 5 µm.

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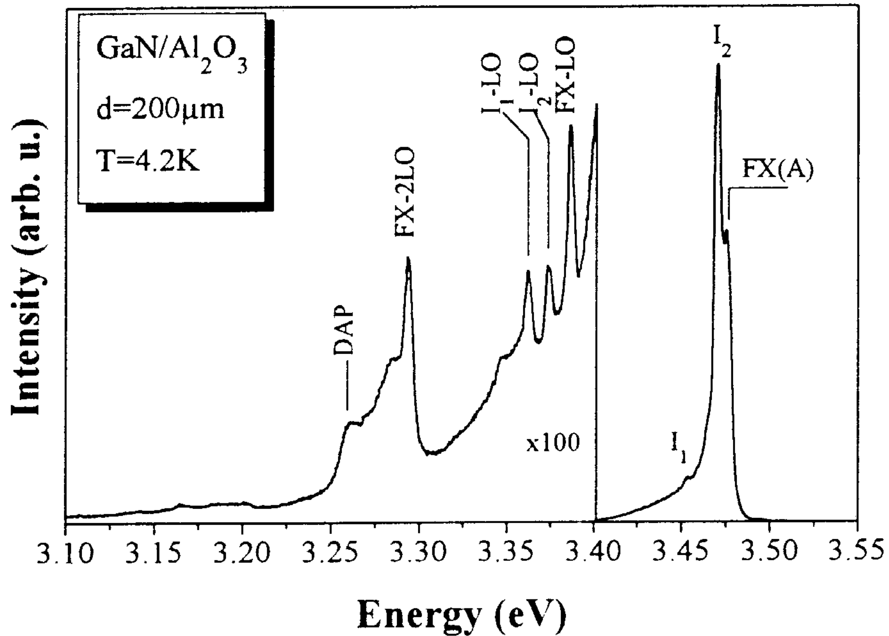

Fig. 1: Low-temperature micro-photoluminescence spectrum taken near the surface. Excitation wavelength was at 325 nm.

Micro-Raman measurements were carried out with a triple-grating Dilor spectrometer and the 514.5 nm line of an Ar^+ laser for excitation. The spatial resolution was better than 1 μm, and we were able to detect Raman shifts smaller than 0.1 cm^{-1}.

Both, photoluminescence and Raman measurements were performed at low temperatures (4.2 K) using a microscope cryostat.

RESULTS AND DISCUSSION

Photoluminescence overview

Figure 1 shows as an overview a low-temperature micro-photoluminescence spectrum taken near the surface in a distance d = 200 μm away from the substrate interface where we assume bulk-like conditions. The spectrum is dominated by the free-exciton emission (FX(A)) located at 3.477 eV and the neutral-donor-bound-exciton emission (I_2) at 3.471 eV. The weak structure near the I_2 at 3.450 eV is due to the annihilation of excitons at neutral shallow acceptors (I_1) [5]. The low-energy side of the spectrum exhibits the phonon sidebands of these excitons. The strength of the second LO replica of the free excitons and the weakness of the donor-acceptor-pair luminescence indicate the excellent quality of the layer near the surface.

Spatially-resolved photoluminesence measurements

The energetic positions of all photoluminescence transitions described above depend on the distance to the substrate surface as can be seen, e.g., for the excitonic transitions from the linescan shown in Fig. 2. In this linescan which was taken in 5 μm steps across the entire GaN cross section we normalized the spectra to their maximum intensity.

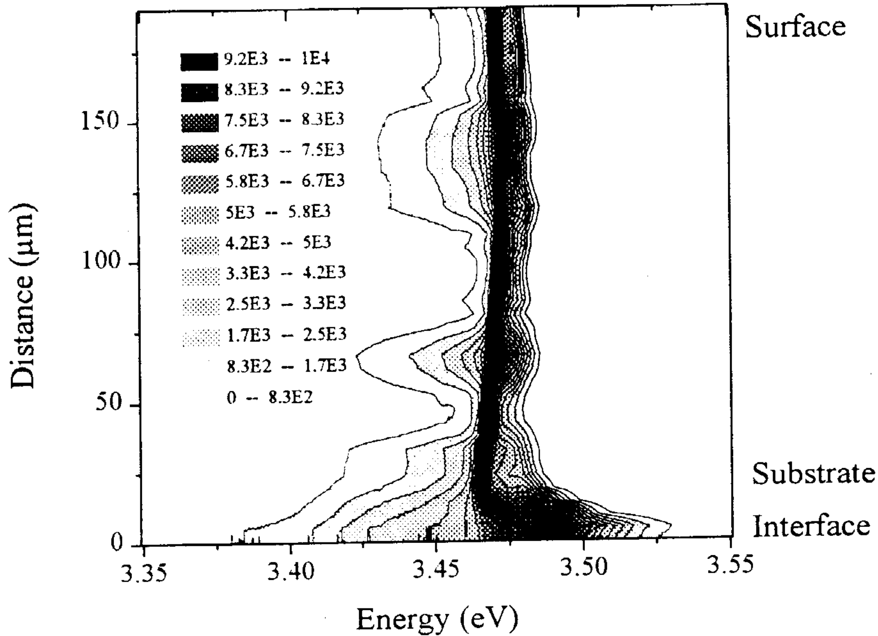

Fig. 2: Depth-profile of the near-bandgap luminescence in a 200 µm thick GaN layer grown on sapphire taken at low temperatures (4.2K) after excitation at 325 nm.

Starting from the surface of the layer (distance d = 200µm) and proceeding in the direction of the substrate interface (d = 0 µm) one can see that the peak position of the excitonic photoluminescence remains nearly constant during the first 100 µm. From d ≈ 100 µm to d ≈ 30 µm the spectra exhibit a small red shift. Proceeding further in the direction of the substrate interface the red shift gives way to a significant blue shift. The corresponding spectra are shown separately in Fig. 3. For clarity the peak positions of the I_2 and of the free-exciton emission are plotted as a function of the distance to the substrate (Fig. 3, right). For the I_2 emission we observed a red shift of 8 meV in total and a blue shift near the substrate interface of about 5 meV. The free-exciton emission follows the I_2 up to a distance of d ≈ 50µm, indicating a constant binding energy of the neutral-donor-bound excitons. For distances smaller than 50 µm this emission shifts strongly to higher energy reaching a maximum blue shift of 21 meV. Consequently the energy difference between both near-bandgap transitions increases.

Spatially-resolved Raman measurements

In order to scrutinize wether this strong blue shift is caused by stress in the GaN layer due to the mismatch of the lattice constants and the thermal expansion coefficients between layer and substrate, we performed micro-Raman measurements of the same spatial region in the layer investigated by photoluminescence measurements. Our measurements reveal that the non-polar E_2 Raman mode exhibits a shift in this region of 0.8 cm^{-1}. This is displayed in Fig. 4 where we plotted the Raman shift of this mode as a function of distance to the substrate interface. We found that the biaxial compressive stress in the layer reduces exponentially with increasing distance from the substrate. The layer is already largely relaxed at a distance d ≈ 30µm away from the substrate. For distances d > 100µm the layer is fully relaxed. This observation is in

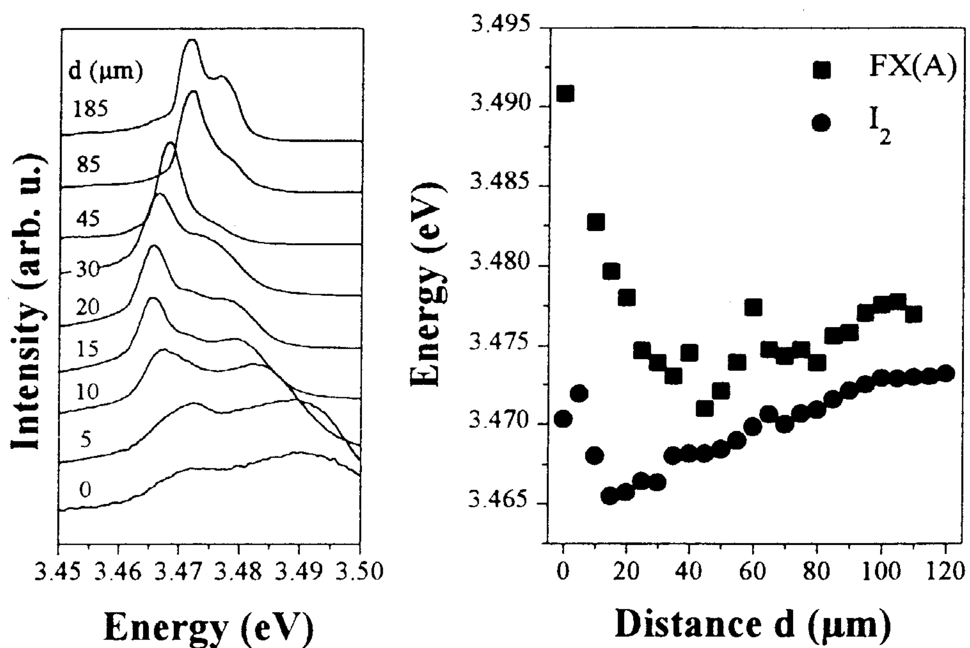

Fig. 3: Low-temperature photoluminescence spectra taken at different distances from the substrate interface (left). Energy positions of the excitonic transitions as a function of distance from the substrate (right)

good agreement with X-ray diffraction measurements on a series of GaN layers also grown on sapphire with varying thicknesses [6].

The observed blue-shift of the near-bandgap luminescence cannot totally be explained by a strain-induced change of the bandgap. According to the relation $\sigma=\Delta\omega/6.2\text{cm}^{-1}$ reported by Kozawa et al. [7], where σ is the biaxial compressive stress in GPa and $\Delta\omega$ is the Raman shift in cm^{-1}, we can quantify the strain in our sample. Rieger et al. [8] investigated the luminescence shift due to biaxial compressive stress and determine $dE_{PL}/d\sigma$ to be between 21 and 27 meV/GPa. Using both relations one would expect a maximum blue shift in our sample of about 3.5 meV.

In fact this change is in the order of the shift we observed for the neutral-donor-bound exciton emission (I_2). However we point out that the free-exciton emission band shift with 21 meV is much too strong to be explained solely by stress in the GaN layer.

This emission band cannot be due to the recombination of free excitons; otherwise the

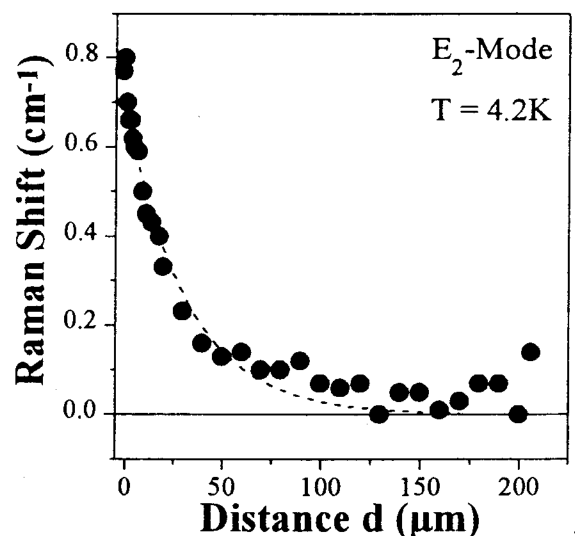

Fig. 4: Shift of the E2-Raman mode as a function of the distance from the substrate interface.

binding energy of the donor-bound-excitons would grow extremely near the interface. We rather think that from the distance at which both, the peak positions of the I_2 and those of the free-exciton emission diverge band-to-band transitions appear. These transitions appear whith increasing doping level and they are known from doped GaN layers or layers of poorer quality [5]. This can be confirmed when considering the intensity of the donor-acceptor-pair luminescence in this layer. As can be seen from Fig. 5 its intensity increases strongly for distances smaller than d < 100μm, indicating that with decreasing distance to the substrate more and more impurities are built in which yields sufficient concentration of impurities to a blue shift of the emissions. The broadening which is also found in the spectra is an additional confirmation.

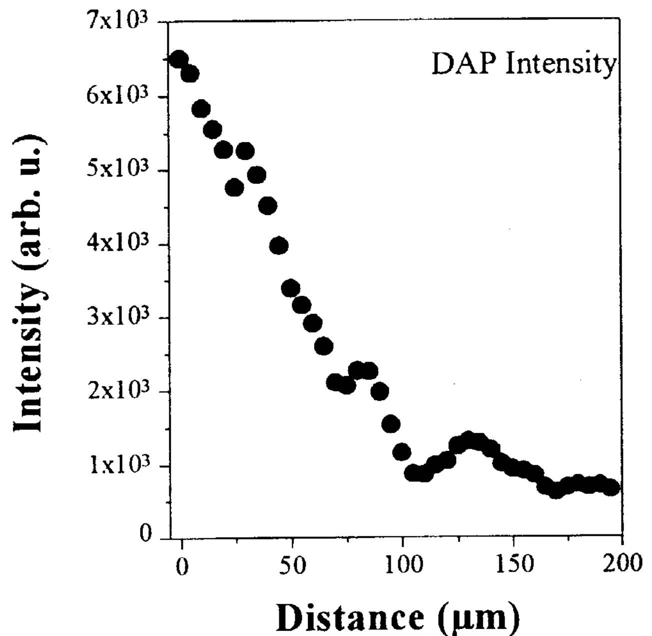

Fig. 5: Peak intensity of the donor-acceptor-pair (DAP) luminescence as a function of distance to the substrate (left).

SUMMARY

We have shown that the photoluminescence of GaN depends strongly on the distance to the substrate interface. Near the substrate we observed a significant blue shift of the near-bandgap emission. Although our micro-Raman measurements reveal that in the same spatial region the biaxial compressive stress in the layer reduces exponentially with increasing distance from the substrate, the blue shift of the photoluminescence with 21 meV is much too strong to be explained solely by stress. We found that with decreasing distance from the substrate the free exciton emission gives way to band-band-transitions, which appear because of the increasing impurity concentration near the substrate.

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REFERENCES

1. For a review see for example: S. Strite, M. E. Lin, and H. Morkoç, Thin Solid Films **231**, 197 (1993)
2. H. Siegle, P. Thurian, L. Eckey, A. Hoffmann, C. Thomsen, B. K. Meyer, H. Amano, I. Akasaki, T. Detchprohm, K. Hiramatsu, Appl. Phys. Lett. **68**, 1265 (1996)
3. F. A. Ponce, D. P. Bour, W. Götz, P. J. Wright, Appl. Phys. Lett. **68**, 57 (1996)
4. For a survey of Raman scattering in GaN see for example: H. Siegle, L. Eckey, A. Hoffmann, C. Thomsen, B. K. Meyer, D. Schikora, M. Hankeln, K. Lischka, Solid State Commun. **96**, 943 (1995)

5. A. Hoffmann, in: Festkörperprobleme, ed. by R. Helbig, Advances in Solid State Physics **35**, (Vieweg, Braunschweig/Wiesbaden 1996), in print
6. K. Hiramatsu, T. Detchprohm, I. Akasaki, Jpn. J. Appl. Phys. **32**, 1528 (1993)
7. T. Kozawa, T. Kachi, H. Kano, H. Nagase, N. Koide, K. Manabe, J. Appl. Phys. **77**, 4389 (1995)
8. W. Rieger, T. Metzger, H. Angerer, R. Dimitrov, O. Ambacher, M. Stutzmann, Appl. Phys. Lett. **68**, 970 (1996)