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Optical properties and transport in PLD-GaN

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Abstract

We present structural, optical and transport data on GaN samples grown by hybrid, two-step low temperature pulsed laser deposition. The band gap of samples with good crystallinity has been deduced from optical spectra. Large below gap band tails were observed. In samples with the lowest crystalline quality the PL spectra are quite dependent on spot laser incidence. The most intense PL lines can be attributed to excitons bounded to stacking faults. When the crystalline quality of the samples is increased the ubiquitous yellow emission band can be detected following a quenching process described by a similar activation energy to that one found in MOCVD grown samples. The samples with the highest quality present, besides the yellow band, show a large near band edge emission which peaked at 3.47 eV and could be observed up to room temperature. The large width of the NBE is attributed to effect of a wide distribution of band tail states on the excitons. Photoconductivity data supports this interpretation.

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1. Introduction

Gallium nitride (GaN) is one of the base materials for modern electronic and optoelectronic devices like light emitting diodes (LEDs), solar blind UV detectors, laser diodes (LD) or high mobility electron transistors (HEMT) [1]. Despite of the impressing technical advances, some basic materials issues remain to be solved. One is the elevated density of unwanted impurities which appear in the material independently of the deposition technique. The MOCVD technique, for instance, relies always on a precursor gas which introduces unwanted effects.

We presented recently a new approach to deposit GaN films, a hybrid, two-step low temperature pulsed laser deposition (PLD). In this work we study optical properties and transport in GaN deposited by this technique. X ray diffraction spectra, optical spectroscopy, photoluminescence and photoconductivity measurements are presented.

2. Experimental details

The experiments were carried out with a set of GaN samples which were deposited at approximately 600 °C on a pre-nitridated sapphire substrate in a two-step cyclic process. In a first step, the gallium is evaporated with the focused fundamental line of a 1.064 μm Nd–YAG laser from a liquid gallium target onto the substrate. During the second step the sample is treated in an atmosphere of high purity nitrogen. Process parameters were optimized at 600 °C. Details about the deposition technique are described elsewhere [2].

The X-ray diffraction (XRD) spectra were measured with a Siemens D5000 diffractometer. PL measurements were carried out with a 325 nm CW He–Cd laser and the excitation power density was typically less than 0.6 W cm^{-2}. A 325 nm band pass filter was used to attenuate lines other than the 325 nm laser line. PL was measured at temperatures between 14 and 300 K using a closed

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cycle helium cryostat. The luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200/mm) and detected by a Hamamatsu R928 photomultiplier.

Coplanar ohmic indium contacts, annealed at 380 °C, were made for the electrical measurements. For transient photocurrent measurements, pulsed excitation was carried out with the second (532 nm) and the fourth harmonic (266 nm) of Nd:YAG laser pulses of 5 ns duration. Pulse energies varied from 4 to 40 μJ at a repetition rate of 10 Hz.

3. Results and discussion

3.1. Structural characterization

The XRD spectra show the (0 0 0 2) peak of hexagonal *c*-axis GaN (Fig. 1) with an FWHM which is (for most samples) below the resolution limit of our XRD unit. An improving sample quality can be concluded from the cps counts. The first samples did not show any appreciable spectra, which we attribute to a higher amorphous fraction of the films. Some samples show several crystal orientations (see Fig. 1, below).

The sample thickness was measured by profilometry and optical interference fringes. Due to a low deposition rate of about 0.1 μm/h, sample thicknesses of the order of 100 nm have to be taken into account for the interpretation of some experiments. The surface morphology was investigated by atomic force microscopy (not shown here). We find overall flat surface morphology with widely distributed inhomogenous features, on different scales. We attribute this to the inclusion of gallium droplets during the deposition process.

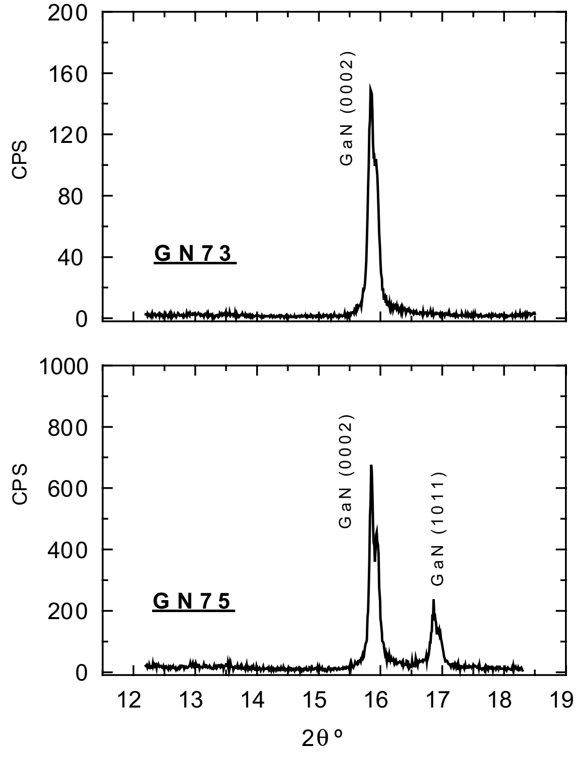

Fig. 1. X ray diffraction spectra from sample GN73 and GN75.

3.2. Optical spectroscopy

The improvement of the optical quality of the samples can be inferred from the optical transmission (Fig. 2) and reflection spectra and is in accordance with the crystalline quality as estimated from XRD.

The tail on the high energy side is due either to finite thicknesses (of the order of 100 nm), to inferior crystalline fraction, or to the presence of small optical pinholes. The band edge is not as abrupt as expected for high quality epitaxial or polycrystalline GaN. As we integrate over the illuminated sample area, the signal includes contributions of unwanted phases as amorphous or cubic GaN as well as metallic GaN droplets. A broad shoulder is observed on the low energy side which arises from transitions involving the band tail states in GaN. According to the presently modest sample quality excitonic effects are not expected. The most appropriate way to evaluate the optical band gap is a fit of the experimental spectral absorption data with a sigmoidal formula which accounts for the characteristic broad rising edge and plateau region:

$$\alpha(E) = \alpha_0/\{1 + \exp(E_G - E/E_{\mathrm{Urb}})\}$$

For the sample GN75, we obtain reasonable values of 3.42 eV for the optical band gap energy E_G, and of 110 meV for the Urbach tail energy E_{Urb}.

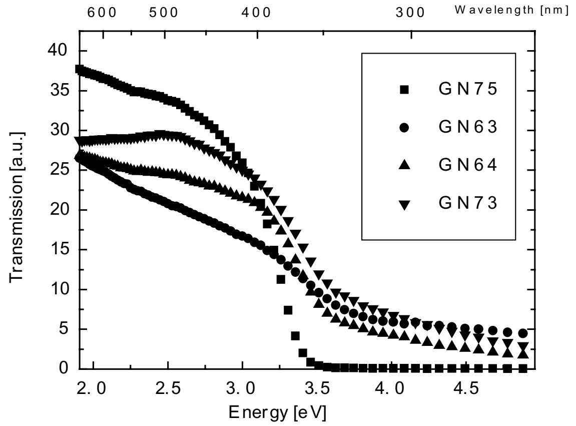

Fig. 2. Transmission spectra.

3.3. Photoluminescence

Photoluminescence is an excellent characterization tool for samples with inhomogeneities on different scales. In Fig. 3 a low temperature PL spectra of the samples with modest crystalline quality is presented. Broad emission bands both in the yellow and red region mainly dominate the observed PL spectra. Moreover the luminescence is quite dependent on spot laser incidence pointing to a heterogeneous defect distribution. In Fig. 4 the temperature dependent PL spectra under above band gap excitation is shown for the GN64 sample. In the presented spectra the shoulder on the low energy side corresponds to the grating blaze angle.

The spectrum is dominated by a broad yellow emission band with a maximum at 2.3 eV and a FWHM of 500 meV which shows a weak thermal quenching for temperatures up to about 80 K.

The yellow emission is typically observed even in high quality GaN samples grown by different processes. To our knowledge this is the first time that the characteristic yellow emission is observed in GaN samples grown by PLD pointing to a natural sequence of grown samples with undesired defects but present in almost all GaN thin films. The temperature dependence of the integrated intensity of the yellow emission band is described by an activation energy of 20 ± 2 meV for the de-excitation processes. This value is in agreement with previous reported values [3] within the temperature region analysed which is an indication that an effective-mass donor is involved in the radiative transition. However, our experiments do not tell anything about the type of the deep level or about the nature of the defects.

Besides the yellow luminescence we identified in samples with low crystal quality two narrow PL lines I3 and I4 peaked at 3.368 and 3.304 eV at 14 K which are currently assigned to strongly localized excitons in literature [4]. The origin of the strong exciton localization is associated to stacking faults which act in GaN as deep donors with activation energies about 150 meV.

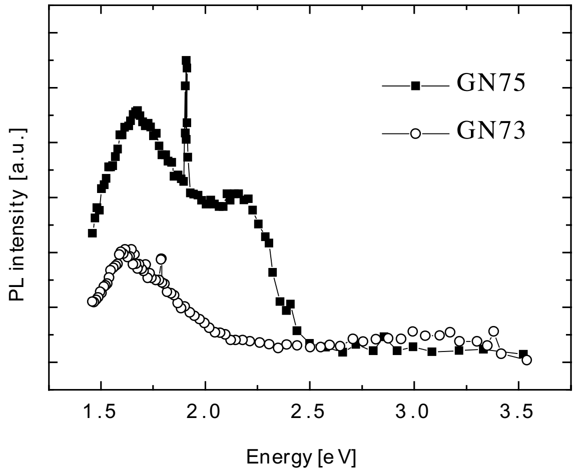

Fig. 3. Typical 14 K PL for medium crystal quality.

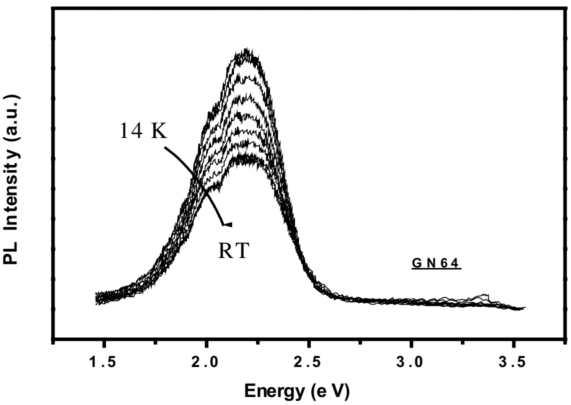

Fig. 4. Temperature dependence of yellow luminescence in GN64.

In samples of higher crystal quality we observe clearly a large near band emission (NBE) with a FWHM of about 200 meV at 14 K, which has been reported also in other PLD-grown GaN films [5]. The spectra of GN96 sample is presented in Fig. 5. It must be pointed out that the large NBE peak could be detected up to room

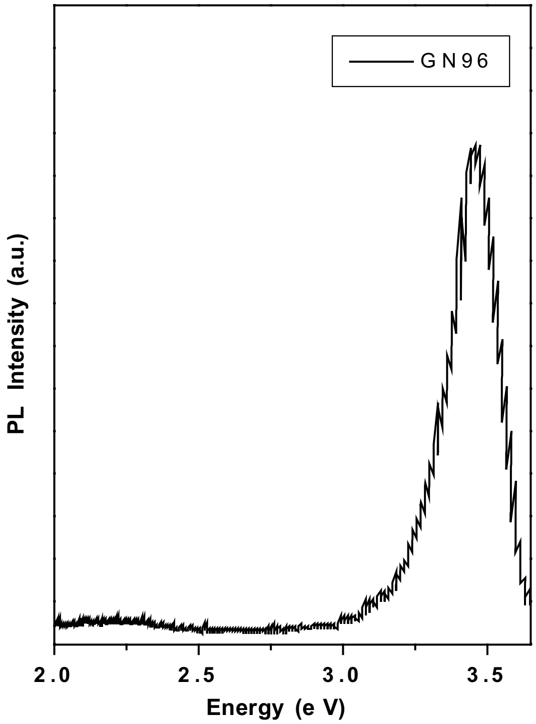

Fig. 5. NBE of GN96 at 14 K.

temperature which indicates that by improving the parameters high quality GaN growth could be achieved. Typical DX and FX transition in high quality GaN layers are very narrow at this temperature. Several aspects could be accounted for the large FWHM NBE emission observed in PLD-grown samples, as for example an overlap of emission bands, the effects of nitridation of sapphire, the target purity, elevated carrier concentration, or a rough crystal surface. However, a dramatic increase of the FWHM may be most likely attributed to the effect of the band-tail states on the exciton peaks in GaN [6]. Besides of the increase of the FWHM to hundreds of meV also the shift of the exciton energetic position is influenced by the band tail. This effect can be described by a modified Varshni equation [7]:

$$E_x(T) = E_x(0) - \alpha T^2/(\beta + T) - \sigma^2/k_B T$$

Here, α and β are the thermal Varshni coefficients, T is the absolute temperature, k_B the Boltzmann constant, and σ the square root of the dispersion of a gaussian type band tail. Hence, the amount of the exciton redshift is enhanced with the dispersion of the tail states.

3.4. Dark- and photoconductivity

The typical dark resistivity at room temperature is of the order of 0.1 Ωcm. For high quality samples, this values would be typical for weak (unintentional) doping and defect-scattering limited bulk transport. With respect to our samples, we attribute this value to a possible porous or non-compact structure of the film.

Even for low crystal quality samples the secondary photocurrent transient showed a slow decay reaching the ms time region after both green and UV laser excitation as shown in Fig. 6. The exponents in the power law decay are around −0.25 which is a typical value for GaN [8,9]. Similar phenomena with different values for the power law index occur in amorphous semiconductors like a-Si:H. As an explanation for long times the presence of extended band tail states was invoked [10]. In our case, the decay extends even to times of thousands of seconds (not shown here), the persistent photoconductivity effect. The origin for this order of magnitude has to be attributed to deep defects.

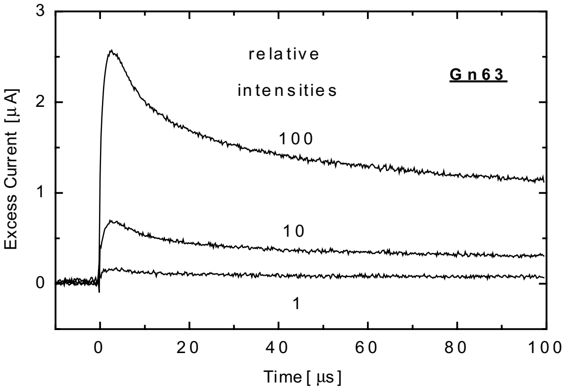

Fig. 6. TPC of GN63.

We measured the photoconductivity frequency dependence below band gap excitation and observed that the decay is slower as $1/f$ as one would expect if only one lifetime would be dominant. This as the previous photoconductivity data support an interpretation in terms of a broad distribution of lifetimes.

4. Summary and conclusion

We presented structural, optical and transport data on GaN samples grown by low temperature PLD. Samples were classified in terms of crystal quality as obtained from XRD. The band gap of samples with good crystallinity has been deduced from optical spectra. Large below gap band tails were observed. In samples with the lowest crystalline quality the PL spectra are quite dependent on spot laser incidence. The most intense PL lines can be attributed to excitons bounded to stacking faults. When the crystalline quality of the samples is increased the ubiquitous yellow emission band can be detected following a quenching process described by a similar activation energy to that one found in MOCVD grown samples. The samples with the highest quality present, besides the yellow band, show a large near band edge emission peaked at 3.47 eV that could be observed up to room temperature. This indicates that by improving the growing parameters high quality GaN could be achieved by PLD-CVD. The large width of the NBE was attributed to the effect of a wide distribution of band tail states on the excitons. Photoconductivity data supports this interpretation.

Acknowledgements

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