Photoluminescence decay in the ps time regime and structural properties of pulsed-laser deposited GaN

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Abstract

In this work we focus on the study of the fast photoluminescence decay in the ps time regime in comparison with structural properties of GaN films deposited by a cyclic pulsed laser deposition technique. Structural film properties are obtained from X-ray analysis and atomic force microscopy. Steady-state photoluminescence performed at 13 K shows the typical donor-bound excitonic transition (D\textsuperscript{0}X) at 3.47 eV and a line near 3.42 eV which can be related to structural defects. Fast fluorescence decays were obtained after excitation at 287 nm (4.32 eV) with 5 ps pulses from a frequency-doubled cavity-dumped dye laser. At room temperature the decay of the blue fluorescence at 367 nm showed decay times between 4 and 40 ps, whereas the yellow contribution at 530 nm could best be described by a multi-exponential fit with decay times of several ns. The results are compatible with published exciton decay times in epitaxial MOCVD-grown GaN films.

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1. Introduction

GaN and related materials have been intensively studied in recent years. This is especially true since the dawn of the first super-bright high-efficiency blue LEDs based on nitride structures [1]. Despite important advances in this field, most of the GaN is usually grown on substrates, which exhibit a large degree of lattice and thermal mismatch, resulting in films with a high density of structural defects such as grain boundaries, dislocations and point defects. These defects normally reveal themselves as electronic states in the forbidden band gap and take part in the characteristic yellow luminescence (YB) present in most of the deposited GaN films. As previously reported [2], the YB-related states have a preference for grain boundaries instead of bulk material. This is particularly important in polycrystalline GaN. Here, smaller surface-to-volume ratio of the grains is desirable in order to reduce the surface grain boundaries where the YB may develop. It was found that the

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stronger the yellow emission, the shorter the exciton photoluminescence (PL) decay time [3]. Also, a shorter PL decay time than theoretically predicted can be attributed to nonradiative relaxation processes like multiphonon emission, deep centres, Auger effect, in competition with the radiative channel.

In this report, we present results on time-integrated photoluminescence (cw-PL), time-resolved photoluminescence (TRPL), surface morphology and X-ray analysis of polycrystalline GaN films deposited by cyclic-pulsed laser deposition (PLD).

2. GaN deposition by hybrid PLD-CVD technique

The GaN thin films were deposited with cyclic-PLD on sapphire substrates [4]. In this method, the liquid Ga target is ablated with a Nd:YAG laser, operated at 1064 nm, 5 Hz, 10 mJ and 5 ns per pulse. After degassing the substrates at 800°C for 1 h under vacuum, nitridation of the sapphire substrates was done with the help of a nitrogen RF plasma set at 13.56 MHz, 1 mbar, 6 W, and for 4 h at 200°C. Then, a GaN buffer layer was grown at 400°C during 15 min (aprox. 20 nm thickness). The film growth was done at 650°C in a cycle composed of two steps. In the first step, the Ga is ablated for 15 s under a 10 W, 1 mbar nitrogen RF plasma. In the second step, the laser is stopped for 5 s in order to incorporate the possibly missing nitrogen. The cycle was repeated for 5 h and the deposition rate varied from 0.06 to 0.08 μm/h.

Crystal orientation of the as-grown GaN films was analysed by a Siemens D 5000 X-ray diffractometer in a θ–2θ configuration equipped with a Mo source. The X-ray diffraction scan presented in Fig. 1 shows that the growth of the films is clearly c-axis oriented. The magnitude of the (0002) peak and the absence of the (10.0) and (10.1) peaks suggests a high degree of texture for both films.

Surface morphology of the films was investigated by atomic force microscopy (AFM). Fig. 2 shows the surface morphology of a PLD-deposited GaN thin film which has a grain-like structure where the grains approach hexagonal shape. The average grain size is 250 nm. Detailed analysis of Fig. 2b reveals a surface roughness of 1.79 nm rms on top of an individual grain.

3. Steady-state photoluminescence (cw-PL)

Steady-state PL measurements were carried out with a 325 nm cw He-Cd laser at temperatures between 14 and 300 K using a closed-cycle helium cryostat. The luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200 mm−1) and detected by a Hamamatsu R928 photomultiplier. In one of our best samples prepared so far, we found, apart from the yellow luminescence band (YB) around 530 nm, several peaks in the near band edge region (NBE), as given in Fig. 3. This sample is characterised by the presence of the donor-bound exciton transition (D0X) at 3.47 eV and a line near 3.42 eV. These lines show a FWHM of 20 and 30 meV at 13 K, respectively. The 3.41–3.42 eV line, commonly seen in samples grown by different methods, has been attributed either to a free-to-bound exciton related with O [5], an exciton bounded to stacking faults [6], or to structural imperfection and rough surface morphology [7]. In low-temperature PLD grown layers, few published PL results are available. For example in Ref. [8], only the I3 and I4 lines related to strongly localised excitons were reported, while in Ref. [9], the authors found the D0X recombination at 3.47 eV, the 3.41 eV and the DAP recombination at 3.27 eV.
4. Time-resolved photoluminescence (TRPL) in the ps region

Time-resolved picosecond fluorescence intensity decays were obtained by the single-photon counting method with laser excitation. The apparatus consisted of a mode-locked Coherent Inova 400-10 argon-ion laser that is synchronously pumped by a cavity-dumped dye laser, delivering 5 ps pulses (with about 20 nJ/pulse) at a repetition rate of 1.7 MHz. The dye laser output beam was frequency doubled in a BBO crystal with an efficiency 5%. Intensity decay measurements were made using a Jobin–Yvon HR320 monochromator and a Hamamatsu 2809U-01 microchannel plate photomultiplier. The instrument response function had effective FWHM of 35 ps. For the low-temperature experiments we used an Oxford cryostat with quartz windows.

As an example, in sample GN128, after excitation with laser pulses at 287 nm (4.32 eV) we can best fit the “blue” fluorescence at $\lambda = 367$ nm (3.38 eV) to a bi-exponential decay with characteristic times $\tau_1 \approx 4$ ps and $\tau_2 \approx 40$ ps. The decay time $\tau_1$ is very close to the overall time resolution of the system of about 5 ps. The respective weights are 83% and 17% for the $\tau_1$ and $\tau_2$ components. Fig. 4 shows that the characteristic decay times increase when moving from the blue to the green-yellow spectral region.

The decay of the “yellow” fluorescence at the wavelength of 530 nm (2.33 eV) is shown in Fig. 5. At 77 K the decay is only slightly slowed down with respect to the room temperature results. For all samples the intensity of the “yellow” fluorescence was much lower than the “blue” luminescence. The decay looks very complex: Only the four-exponential decay with characteristic times $\tau_1 = 36$ ps, $\tau_2 = 170$ ps, $\tau_3 = 660$ ps and $\tau_4 = 3.366$ ns gives a good fit. Besides the “yellow” fluorescence, all samples have a component with a very long characteristic time $> 200$ ns that cannot be measured in our experimental conditions.
5. Discussion and summary

Our PLD samples usually show an inhomogeneous surface structure in the AFM pictures. This can probably explain why the relative PL band contribution in cw-measurements depend on the particular spot chosen on the sample surface. We have not observed the free exciton emission peak expected at 3.48 eV for high-quality GaN samples. However, our films are still very thin and lack a considerable buffer layer. Also, we have not yet done measurements at liquid helium temperatures.

In Table 1 we have summarised the observed decay times in the ps range for different temperatures. Using literature values from the work of Eckey et al. [10] we have assigned the 4 ps time to the decay of a free exciton, FX, and the 40 ps component to the decay of the neutral donor-bound exciton, D0X. Furthermore, ps decay data are reported in Ref. [3] and are consistent with our results.

We have also tried to represent the experimental data in a double-logarithmic plot. In particular, the YB emission can be described by a power-law function instead of the multi-exponential decay. The power law has an exponent of $m = -1.3$. The power law approach is another way to say that we have to deal with a broad distribution of decay times.

As far as time-resolved photoconductivity (TPC) is concerned we have found in many cases that the decay fits quite well to a power-law assumption. The exponent is of the order of $-0.3$ to $-0.5$ and was explained with a broad density-of-states distribution. Those trap states would lie far below the band edges as indicated by the large decay times [11]. However, the photocurrent decay

![Fig. 4. Photoluminescence decay measured at different emission wavelengths after excitation with a 5 ps pulse at 287 nm (4.32 eV).](image1)

![Fig. 5. Decay of the yellow luminescence (YB) measured at 2.3 eV after excitation at 4.32 eV at room temperature and at 77 K.](image2)

| Table 1 | Tentative attribution of the partial components of our multi-exponential fit comparing the respective decay times with literature values |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 300 K 367±30 nm | 77 K 362±30 nm  | 2 K 20±5 ps      | Assignment      |
| 1 4 ps           | This paper      | This paper      | 20±5 ps         | Free exciton   |
| 2 40 ps          | 9 ps            | 34±5 ps         | D0—neutral donor bound exciton |
| 3 —              | 42 ps           | 160±15 ps       | 11—neutral acceptor bound exciton |
| 4 —              | 140 ps          | 370±40 ps       | 11′—neutral acceptor bound exciton |
characteristics give no hint as to the nature of the implied deep states. Another handicap is the limited time range, starting at several hundred ns in our case as compared to tens of ps for transient photoluminescence.

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