Non-radiative and radiative properties of PLD-deposited polycrystalline GaN studied by UV ps-to-ns laser pulses

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Abstract

We have applied short laser pulses with a minimal pulse width of 5 ps to study the non-radiative and radiative carrier density decay in polycrystalline GaN. The GaN films are deposited by a cyclic pulsed laser deposition (PLD) technique at a relatively low substrate temperature of 600 °C on sapphire substrates. Results from photoluminescence decay and transient photocurrents are compared with respect to trapping, recombination, and transport of photogenerated carriers in polycrystalline GaN thin films. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Epitaxial films of GaN, usually grown by MOCVD at high temperatures near 1000 °C, and its alloys are important materials for light-emitting devices like blue-UV lasers and LEDs, short-wavelength optical detectors and high-temperature electronics. However, the presence of unwanted deep states in the band gap due to native or extrinsic defects reduces the efficiency of devices. Those defects have been correlated with the yellow band (YB) near 2.3 eV observed in photoluminescence and discussed in detail in the literature [1,2]. One of the reasons of the appearance of such deep states is the fact that 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. This should apply in particular to our polycrystalline GaN films deposited at relatively low substrate temperature of 600 °C.

In this report, we present results on surface morphology, time integrated photoluminescence (cw-PL), time resolved photoluminescence (TRPL) and transient photoconductivity (TPC) of polycrystalline GaN films deposited by Cyclic-PLD.

2. Cyclic PLD GaN films and structural characterization

The GaN thin films were deposited with Cyclic-PLD on sapphire substrates [3]. 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. 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 (ca. 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 during 5 h and the deposition rate varied from 0.06 to 0.08 l/m/h.

X-ray diffraction scans show that the growth of the films is clearly c-axis oriented. The magnitude of the (0 0 0 2) peak and the absence of the (10.0) and (10.1) peaks suggest a high degree of texture for both films. Surface morphology of the films was investigated by scanning electron microscopy (SEM). Fig. 1 shows the surface morphology of a PLD-deposited GaN thin film with a grain-like structure where the grains approach as hexagonal shape. GaN is of wurtzite type, and due to the lattice mismatch between GaN and the sapphire substrate, a three-dimensional island-type growth is observed. The average grain size is around 250 nm. We want to point out that the grains are not fully connected at a film thickness of about 1 µm, and that the surface roughness on a scale of the order of some microns equals approximately the grain size, as measured with atomic force microscopy (AFM). However, on top of an individual grain, we measured a surface roughness as low as 1.8 nm rms, evidencing a flat single grain surface. Photoelectron emission spectroscopy (XPS) shows that our samples are gallium rich near the surface.

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) and detected by a Hamamatsu R928 photomultiplier.

The measured spectra depend on the spot incidence, indicating some non-homogeneity of the sample. However, our findings can be classified into two important spectral regions (Fig. 2): a broad yellow luminescence band (YB), centered at around 530 nm, and several partially unresolved peaks in the near band edge region (NBE), slightly below the room temperature GaN bandgap of 3.4 eV.

Exciton lines are usually interpreted as a sign of high crystal quality. At 13 K, the excitons are bound to neutral shallow donors, giving rise to the donor-bound exciton transition (D0X) at 3.47 eV with an FWHM of 20 meV. The broadening of the low-energy tail is consistent with impurity-band formation and band tailing [8]. The linewidth is indicative of a doping level in the mid 10\(^{17}\) cm\(^{-3}\), which is slightly above the Mott density of 2\(\times 10^{17}\) cm\(^{-3}\); but well below that of degenerate doping at 2\(\times 10^{18}\) cm\(^{-3}\) [9].

A second line near 3.42 eV with an FWHM of 20 meV is usually attributed to structural imperfection and/or rough surface morphology [4].

4. Time-resolved photoluminescence (TRPL) in the ps region

Time-resolved picosecond fluorescence intensity decays were obtained by the single-photon timing 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 1.7 MHz. The dye laser output beam was frequency doubled in a BBO crystal with an efficiency of 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 an effective FWHM of 35 ps. For the low temperature experiments we used an Oxford cryostat with quartz windows.

The room temperature transient NBE in GaN is dominated by exciton dynamics, due to the high binding energy.
energy. As an example, in sample GN128, after excitation with laser pulses at 287 nm (4.32 eV) we can best fit the ‘blue’ fluorescence in Fig. 3 at $k = 367$ nm (3.38 eV) to a bi-exponential decay with characteristic times $s_1 \approx 4$ ps and $s_2 \approx 40$ ps. The decay time $s_1$ is very close to the overall time resolution of the system about 5 ps.

The measured lifetime is a composite of the individual lifetimes of all possible radiative and non-radiative transitions in the spectral window observed. We attribute the fastest individual exponentials to the free exciton, as well as to donor and acceptor bound excitons [5].

Fig. 3 shows that the characteristic decay times increase when moving from the blue to the green–yellow spectral region. In this sample the intensity of the ‘yellow’ fluorescence was much lower than the ‘blue’ luminescence.

The decay dynamics may be understood in a double logarithmic representation. 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 whole distribution of decay times.

5. Transient photoconductivity (TPC) in the ns region

Typical dark resistivity values of 0.1 $\Omega$cm allow to estimate a background carrier concentration of approximately $10^{18}$ cm$^{-3}$, assuming a mobility value near 50 cm$^2$/Vs. Current measurements were performed after excitation by 5 ns pulses of the 2nd (532 nm) and 4th (266 nm) harmonics of a Q-switched Nd:YAG laser. We have found in many cases that the decay fits quite well to a power-law assumption (Figs. 4 and 5). The exponent is of the order of $-0.3$ to $-0.5$ and is explained with a broad density-of-states distribution [6]. The trap states lie far below the band edges as indicated by the large decay times. The exponent is, to a first approximation, independent of the excitation wavelength. Below bandgap and above bandgap light lead to the same decay dynamics (Fig. 4). Up to a critical value, the decay changes only slightly with the excitation energy, getting slower, as shown in Fig. 5. The inset shows that the photocurrent depends sublinearly on the excitation density. The power law index, the so-called Rose-coefficient, is different for the peak and the integrated value of the transient photocurrent with values of 0.6 and 0.7, respectively, indicating a mixture of mono- and bimolecular recombination. The carrier dynamics slow down for higher excitation energies.

6. Discussion and summary

The joint structural SEM, AFM, XRD and XPS data indicate that we have a polycrystalline material, with high quality GaN columns of hexagonal shape and a
lateral diameter of about 250 nm. Therefore, the electronic and some optical properties of the samples will be determined by the grain boundaries rather than by the bulk properties.

The temperature independent power law dependence of the photocurrent and the photoluminescence decay may be conceptually understood on the basis of Seto's model [7], evoking the spatial separation of electrons and holes. A schematic of the model band structure is sketched in Fig. 6. High quality GaN grains with a grain size \( L \) are separated by two-dimensional grain boundaries with midgap surface state. Their origin may be related to interfacial defects or to the inclusion of small gallium droplets. In any case, some of the free majority carriers (electrons) diffuse to the boundary and charge it up, which results in upward bended conduction and valence bands symmetrically to the two-dimensional interface plane. The resulting interface potential repels electrons into the grain center and attracts holes to the grain boundary region. The depletion width depends on the carrier density, and in the case of illumination, it depends strongly on the excitation level. Electron hole pairs can be created inside the grain by above gap light or in the grain boundary region with below gap illumination.

The near band and especially the excitonic emission must originate in regions of high crystalline quality. As only a small number of holes is available in the grain center, the PL NBE emission efficiency is reduced, as observed in our experiments. Additionally, strong reabsorption of the NBE radiation is expected, due to the elevated absorption in the boundary regions. However, the exponential decay dynamics validate the assumption of high optical quality regions. The short lifetimes measured in the ps regime evidence the contribution of excitons up to room temperature. At low temperatures (<20 K), recombination in GaN is governed by bound excitons [9], which is experimentally validated by the peak at 3.47 eV in the 13 K PL spectrum in Fig. 2. At intermediate temperatures – like the 77 K used in the PL decay experiments – free exciton transitions are expected to dominate, unless the attractive field between electrons and holes gets screened by elevated electron background concentration [9]. To validate the correlation of the shortest lifetimes in the 77 K PL decay with free excitons, it is still necessary to reduce the observation bandwidth in the decay spectra or to obtain a cw spectrum at the same temperature. Both topics will be addressed in future work.

Due to the band bending, more electronic trap states are available at the interface when compared to the grain center. The yellow luminescence can then be explained by recombination between spatially separated electrons and holes [10]. At the moment it is not clear if the spatial separation of electrons and holes, which enters the radiative recombination probability (\( \tau^{-1}_{\text{rec}} \)) exponentially, correlates with the dimensions evidenced by the SEM in Fig. 1. More samples and more work is necessary to validate this interpretation. From the functional dependence of the long term PL and PC decay in Figs. 3–5 it is more likely that minority carrier (hole) trapping and reemission dominates the carrier decay at fast and slow times. From this interpretation, momentum conserving transitions in the multiple trapping model indicate quasi-exponential density of states distributions with Urbach energies characteristic for the employed time scale of the experiment.

As a next important step we want to study the correlation of structural and optical properties, for example by means of correlation of cathodoluminescence and SEM data with high spatial resolution.

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