Time-Resolved Photoluminescence Characterization of GaN Layers Grown by Metalorganic Chemical Vapor Deposition

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Abstract. GaN layers with wurtzite structure were found to exhibit intense photoluminescence (PL) at 3.47eV ($T = 10K$) corresponding to recombination of excitons bound to neutral donors. The dependence of this luminescence on the growth conditions, layer thickness and density of excitation power was studied. New PL bands were evidenced in the UV region under high levels of excitation ($I_{exc} \geq 0.56 mJ/cm^2$).

1. Introduction

III-Nitrides are particularly attractive for optoelectronic and electronic applications due to their large bandgap, high thermal conductivity and radiation hardness, which makes them suitable for the “blue” spectrum and high temperature operation. With the recent demonstration of high-efficiency blue LEDs for display applications and laser diodes for digital data read-write applications, it becomes imperative to gain better understanding of the optical properties of nitrides, the associated optical transitions and their origin.

GaN is a direct-gap semiconductor, which crystallizes in wurtzite and zincblende structures. Due to the absence of GaN single crystals of sufficient large dimensions, sapphire is to date the most commonly used substrate in GaN epitaxy. The large lattice mismatch (13%) and difference in thermal expansion coefficient between sapphire and GaN layers result in considerable stress and, therefore, in dense defect generation near the substrate interface as well as in the layer. Recent studies have shown that the generation and propagation of defects into the epitaxial layer may be inhibited, to some extent, by the use of different buffer layers [1,2]. However, the peculiarities of layer morphology, defect content and their influence on physical properties are still under discussion [3].

The goal of this work was to study the radiative properties of GaN layers grown by metalorganic chemical vapor deposition (MOCVD) on sapphire. The layer quality was explored by micro-Raman spectroscopy (RS) and scanning tunneling microscopy (STM).

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2. Experimental

The GaN layers were grown by low-pressure (60torr) MOCVD on (0001) c-plane sapphire using trimethylgallium (TMGa) and ammonia (NH_3) as source materials. A modified EMCORE GS-3200 system was used for this purpose. A buffer layer of ~250Å thick GaN was first grown at ~510°C. The GaN layers grown on top had thicknesses ≥0.9µm and were grown at temperatures ranging from 850 to 1050°C. The characteristics reported in this work refer to four different samples. Samples A and B were grown at a temperature of 950°C and had a thickness of 1.8 and 0.9µm, respectively. Samples C and D were grown at a temperature of 1050°C and had a thickness of 1.25µm.

A pulsed excimer laser operating with a KrF mixture (E_{exc} = 5eV) and 3.8ns pulse duration was employed for time-resolved PL characterization of the GaN layers. Most of the experiments were carried out at an excitation intensity of 56µJ/cm^2. The micro-Raman spectra (RS) were excited with the 514.5nm line of an Ar^+ laser. The scattered light, in a nearly backscattering geometry, was analyzed by a Jobin-Yvon triple monochromator with a spectral resolution of 2cm^{-1}. The STM used in the experiments has been described previously [4].

3. Results and Discussion

The PL spectra of samples studied in this work manifested two bands with maxima in the UV and yellow regions. The high-intensity UV band with the maximum at ~3.4eV (T = 300K) corresponds to near-bandedge transitions while the weaker and wider peak at 2.2 – 2.3eV is related to defect energy levels within the band gap. The latter band, which is practically absent in the PL spectra measured under excimer laser excitation (Fig. 1), was found to become more pronounced when excited by light with the energy correlating to that of the GaN band gap. Nevertheless, even under such conditions the intensity of the so-called “yellow” luminescence was at least three to four orders of magnitude lower than that of the near-bandedge PL.

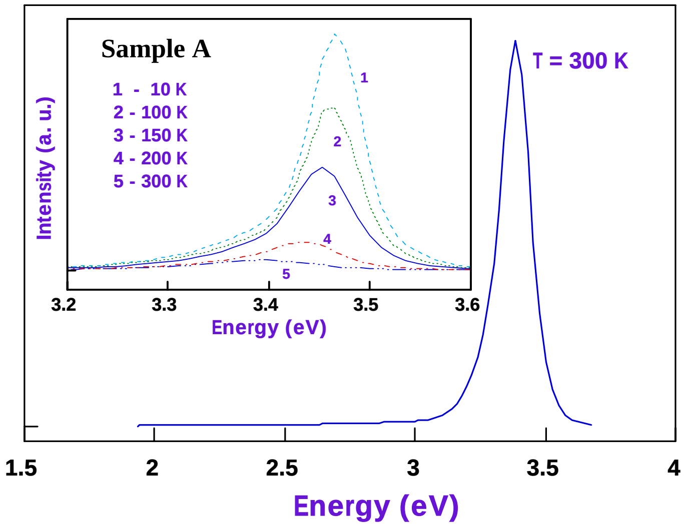

Fig. 1: PL spectrum of sample A at T = 300K. The inset shows the temperature dependence of the near-bandedge PL band.

At 10K the UV PL band is centered at 3.47eV that corresponds to excitons bound to a neutral donor [5]. The inset in Fig. 1 shows typical PL spectra obtained under variable temperature conditions. A gradual low-energy shift of the band accompanied by quenching is observed with increased sample temperature. The PL spectrum obtained at higher temperatures (300K) continues, however, to exhibit a sharp peak as shown at different scale by the spectrum in Fig. 1.

The analysis of time-resolved spectra has shown the UV emission to decay without visible changes in position and shape of the band (Fig. 2). The decay time estimated from these spectra is in the range of several hundred picoseconds, its accurate evaluation is impeded by the relative high pulse duration of the employed excimer laser.

By comparing layers of different thickness it was found that the full width at half maximum (FWHM) of the PL band is smaller in thicker epilayer (see decreased FWHM for thicker layer A in Fig. 3). This suggests a higher crystalline quality in thick epilayers.

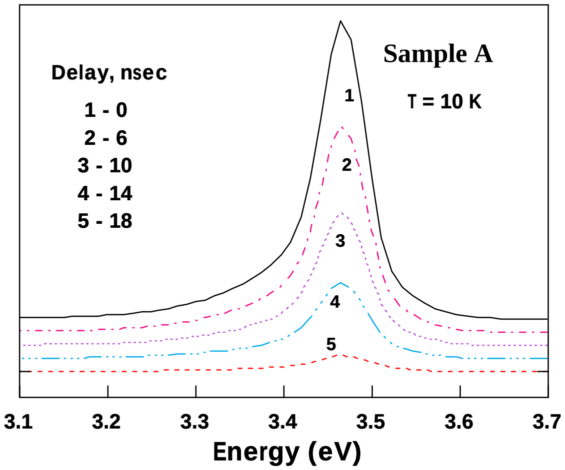

Fig. 2: Time-resolved spectra for sample A.

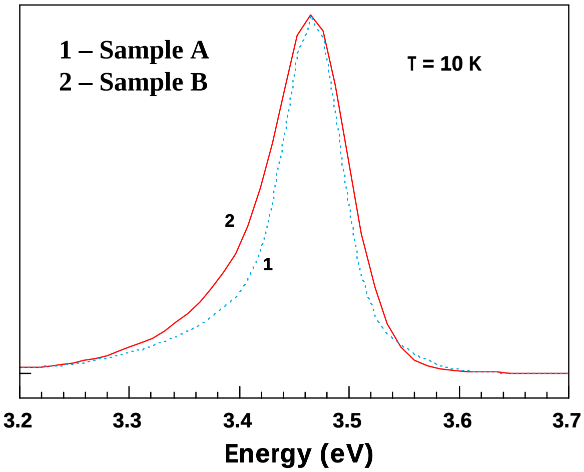

Fig. 3: A comparison of PL spectra for GaN layers with different thicknesses.

Micro-Raman scattering analysis proved the superior crystalline quality of the lattice in thicker epilayers (Fig. 4). In sample A we observed rather strong RS by optical phonons E_2, E_1(TO) and A_1(TO) compared with the thinner sample B. Apart from that, a weak RS peak was observed at about 740cm^{-1} related probably to LO-modes. The occurrence of a weak peak in this region of unpolarized RS spectra is indicative of coupling between LO-phonons and plasmon [6]. We believe that the shoulder at about 520cm^{-1} is also related to the LO-phonon-plasmon coupling (LOPC). It seems to correspond to the low-frequency LOPC mode which is, according to [7], about 11cm^{-1} below the A_1(TO) phonon frequency.

Tests were also carried out for samples grown at higher temperature with variable temperature ramping rate between the buffer and the bulk GaN layer; samples C and D used for this purpose were grown using a ramping time of 10 and 20mins, respectively. These samples show under low excitation densities an additional peak at a photon energy of 3.39eV (Fig. 5, curve 1). Considerable changes in the PL spectra were observed at high excitation intensities ($I_{exc} \geq 0.56$mJ/cm^2). In this case new PL maxima appear and merge in the spectrum between 3.4 and 3.5eV (Fig. 5, curve 4). A superlinear dependence of the PL intensity upon the excitation power density was evidenced for the peaks involved indicating the occurrence of bimolecular recombination between free carriers [8]. The downward frequency shift with increasing excitation intensity may be attributed to local heating of the sample. In contrast to this, the peak at 3.39eV shows an opposite shift with increasing I_{exc} which is indicative of carrier recombination via donor-acceptor pairs. At the same time no visible changes in the PL decay were found with increasing the excitation level.

The full decay of PL in samples C and D was found to be longer than that in samples A and B. The longest decay time was observed in sample D grown at a lower ramping rate. These results are in agreement with STM characterization data. In particular, the surface roughness in sample D was found to equal 4 - 6nm which is nearly two times smaller than in sample C (8 - 10nm).

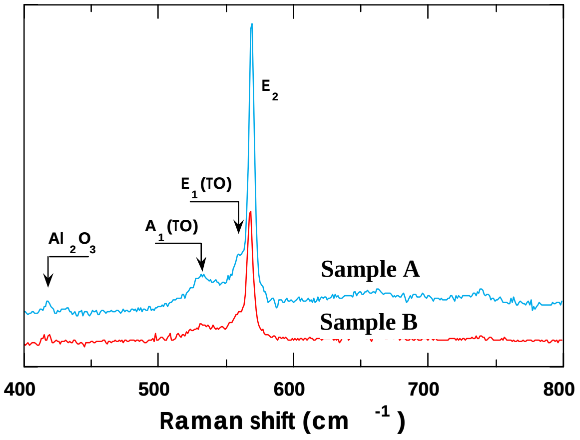

Fig. 4: Micro-Raman spectra for GaN layers with different thicknesses.

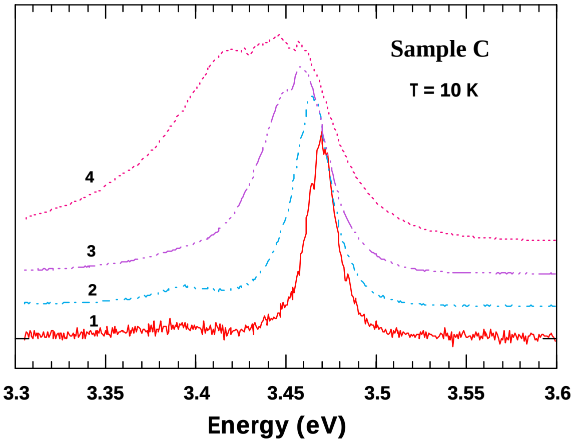

Fig. 5: Near-bandedge PL spectra for sample C at the following excitation intensities: 1) $5.6\mu J/cm^2$; 2) $56\mu J/cm^2$; 3) $0.56mJ/cm^2$; 4) $5.6mJ/cm^2$.

4. Conclusion

An intense luminescence in the UV region was observed in wurtzite-phase GaN layers grown by MOCVD, the low excitation-density PL spectra consisting of one band at 3.47eV related to bound excitons. The characteristics of this band were found to depend on the epitaxial growth conditions. New near-bandedge PL bands were evidenced under high excitation power densities. From PL measurements it follows that the higher the thickness of the epilayer and the longer the ramping time between buffer and bulk growth the better the crystalline quality. Further information about these trends was obtained by complementary RS and STM analysis.

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