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Luminescence and Reflectivity of GaN/sapphire grown by MOVPE, GSMBE and HVPE

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Abstract

This work presents an optical characterization by luminescence and reflectivity of GaN layers grown on sapphire using MOVPE, HVPE and GSMBE. Well resolved optical spectra are obtained for each growth technique. The luminescence of Mg doped MOVPE grown GaN is also studied. A Mg acceptor optical depth of ~ 260 meV is obtained.

1. Introduction.

Three growth techniques are simultaneously investigated in our laboratory for the attainment of electronic quality GaN layers. Hydride Vapor Phase Epitaxy (HVPE), where growth is obtained via the reaction of NH_3 with Ga chlorides (T_g ~ 1030 °C) have been used for a long time, and the first physical investigation of GaN material properties were performed on HVPE grown crystals [1] [2]. HVPE allows large growth rates (30-80 µm/h) and can be used for pseudo-homoepitaxy purposes. Metal-Organic Vapor Phase Epitaxy (MOVPE) uses the reaction of Ga metalorganics (TrimethylGallium in our case) with nitrogen precursors, mainly NH_3 (T_g = 1000-1100 °C) and to date has allowed the attainment of high quality nitride based structures, recently illustrated by the realisation of pulsed mode blue laser diodes operating at room temperature [3]. Gas source molecular beam epitaxy (GSMBE) is a new exploratory technique. Expected advantages should come from the low growth temperatures used (~800 °C) and low gas consumption. Also, the *in situ* characterization tools of MBE are invaluable [4]. In this work an optical characterization of GaN layers grown on (0001) Al_2O_3 by the three above techniques is presented. Temperature dependent photoluminescence (PL) and reflectivity experiments were performed. Due to the importance of strain effects, mainly of thermoelastic origin, in a strongly mismatched system as GaN/Al_2O_3 [5], these two techniques are complementary. Reflectivity, providing intrinsic energy levels, is indeed essential in the interpretation of PL transitions, mainly of extrinsic origin. Well resolved reflectivity spectra, allowing the identification of the three (A, B and C) excitonic levels of GaN, can be obtained, whatever the growth technique [6]. The results will be mainly concerned with nominally undoped samples, but also with Mg doped MOVPE-grown ones.

2. Results and discussion

Figure 1 displays the luminescence spectra at 9 K of three undoped GaN samples grown by HVPE, GSMBE and MOVPE, from top to bottom. The thicknesses are 100, 0.8 and 3 µm respectively. The residual n-type doping is evaluated to ~10^{18} cm^{-3} for HVPE and GSMBE samples and below 10^{17} cm^{-3} for the MOVPE one. The three spectra are dominated by band edge excitonic transitions involving free exciton A, donor bound exciton (I_2, 6 meV lower in energy than A) and acceptor bound exciton (I_1, 10 meV lower than A) recombinations [1] [2] [6]. The energy of all these lines varies (whithin 10 meV in our samples) with the biaxial strain level, and reflectivity spectra are indispensable for the identification of these PL transitions, by providing the energy of the free exciton states. In the 3.27 eV range are observed donor-acceptor pairs (D^0A^0) recombination involving the usual residual donors and acceptors of GaN [7]. Their depths are evaluated to 35±5 and 220±5 meV respectively [6], from an analysis of their excitation intensity dependence [8]. This is in agreement with earlier determinations [7]. Inspection of figure 1 shows that the ratio of band edge to acceptor related transitions increases when going from HVPE to GSMBE to

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MOVPE grown samples, at least at present. This is in agreement with the highest purity measured by Hall effect in MOVPE samples. Of course, in GaN, impurities does not necessarily mean atom impurity.

2.1. MOVPE-grown GaN.

The lower spectrum shown in figure 1 is typical of high purity MOVPE grown GaN. Residual acceptor related luminescence is hardly observed in such samples. Besides band edge excitons, dominated by I_2, low intensity lines (labelled D_1, D'_1) can be observed in the 3.38-3.9 eV range. They are attributed to phonon replica of free exciton luminescence or to free hole-deep donor transitions (or to deeply bound excitons) in which the hole is weakly bound [6]. Due to the low residual n-type doping level, efficient p-type doping using Mg can be achieved, and will be discussed in the following. Figures 2a and 2b display the evolution of near edge luminescence of MOVPE-grown GaN with increasing Mg doping. Also shown is a nonintentionnally doped sample for comparison (the spectrum is equivalent to that shown in figure 1). In a weakly Mg doped sample (G103, still n-type), one notes in addition to the residual (D^0A^0) band and its LO phonon train a new band, ~40 meV lower in energy (labelled D^0Mg^0). With increasing Mg doping (samples G112, G269), this new band dominates the spectra, and simultaneously shifts towards lower energies (figure 2a). Eventually, at larger doping level, the spectrum becomes dominated by a broad 'blue band' peaking at 2.8-2.9 eV, depending on samples, as shown in figure 2b. This behaviour has already been reported [9] [10] [11] and can be due to a deepening of acceptor levels, of donor levels, or both. Figure 3 displays the excitation intensity dependence of the PL peak of the D^0Mg^0 band. In sample G103, the variation of the peak energy can be accounted (solid lines) assuming a 30-40 meV donor and acceptors of ~220 meV (A^0) and ~265±10 meV. This last value is ascribed to Mg^0 acceptors, and is in agreement with refs [12] [13]. As such, we may tentatively assign the series of sharp lines near 3650 Å in the spectrum of sample G103 to close D^0Mg^0 pairs of type I. The D^0Mg^0 transitions are replicated by 90±5 meV phonons with a Huang-Rhys factor S of 1±0.2. With increasing Mg doping level, the shift with excitation intensity of the 3.2 eV donor-acceptor pair band increases (figure 3). This rather suggests the apparition of deep compensating donors. Eventually, deep centers, or band tailing, occur, corresponding to the 'blue band' . Note that such a behaviour is qualitatively similar to that encountered in the luminescence of p-type (nitrogen) doped ZnSe, other wide gap semiconductor. Occurrence of deep compensating donor levels rather than deep acceptor states is in agreement with the fact that the Hall depth of Mg acceptors is 150-170 meV whatever the doping level [9].

2.2. HVPE-grown GaN.

Figure 4 displays the PL and reflectivity spectra of an undoped 100 µm thick HVPE-grown GaN sample. The reflectivity spectrum, with an A exciton energy of 3.472 eV, indicates that the layer is fully relaxed [5]. The various PL transitions observed have been described above. What we shall discuss is the broad pedestal observed on the PL spectrum, extending on the high energy side up to the layer's band gap. On figure 4 is also given the luminescence spectrum recorded from the substrate side. It consists of a broad band, with a high energy cutoff at ~ 3.6 eV. To understand such a line shape, we show in figure 5 the PL and reflectivity spectra of an n^+ ($n = 4\ 10^{19}$ cm^{-3}) HVPE grown sample. The high residual doping level is presumably due to the fact that this sample was grown using ammonia which was not purified by molecular sieves in line. The PL spectrum is also broad, with a large low energy tail, and a rather sharp high energy cutoff well above the pure GaN's band gap. Such spectrum ressemble those of type II or type III GaN, in the terminology of reference [1]. We interpret it as in the case of n^+ GaAs, *i.e.* as due to indirect transitions between acceptor like tail states and electrons up to the Fermi level [14]. In particular, the half-intensity high energy cutoff $E_{1/2}$ agrees with the energy of recombinations between tail-localized holes and Fermi edge electrons $E_g+E_F-E_T$, as expected [14] (figure 4). We then ascribe the broad pedestal observed on the PL spectrum of high purity HVPE-grown GaN (figure 5) to partially reabsorbed PL from an interfacial n^+ layer.

2.3. GSMBE-grown GaN.

As mentionned previously, the high vacuum conditions of MBE allow the use of *in situ* characterization tools. Combining *in situ* Reflection High Energy Electron Diffraction experiments and *ex situ* PL, an optimized sapphire nitridation procedure has been defined [4]. The spectrum of a 8000 Å thick GSMBE grown layer is displayed on figure 1. Besides already discussed transitions I_2 and D^0A^0, to be noted is a band at 3.404 eV and labelled D_2. On another hand, the PL spectra of layers that are only 600 Å thick are dominated by a band peaking at 3.425±0.005 eV [4], and attributed to free hole-oxygen donor recombinations, according to reference [15]. We then tentatively ascribe the D_2 band in the spectrum shown in figure 1 to transitions involving O impurities, the source of oxygen being possibly diffusion from the sapphire substrate.

3. Conclusions.

GaN/Al_2O_3 layers grown using three different techniques, MOVPE, HVPE and GSMBE have been characterized using luminescence and reflectivity experiments. Well resolved reflectivity spectra can be obtained whatever the growth technique, allowing strain effects to be taken into account in the interpretation of the PL spectra. Samples displaying excellent optical quality, with luminescence dominated by sharp band edge exciton lines, have been grown. MOVPE allows at the present stage to grow the highest purity samples. This allows efficient p-type doping by magnesium. An optical depth of 260-270 meV for Mg acceptors is deduced from our characterization.

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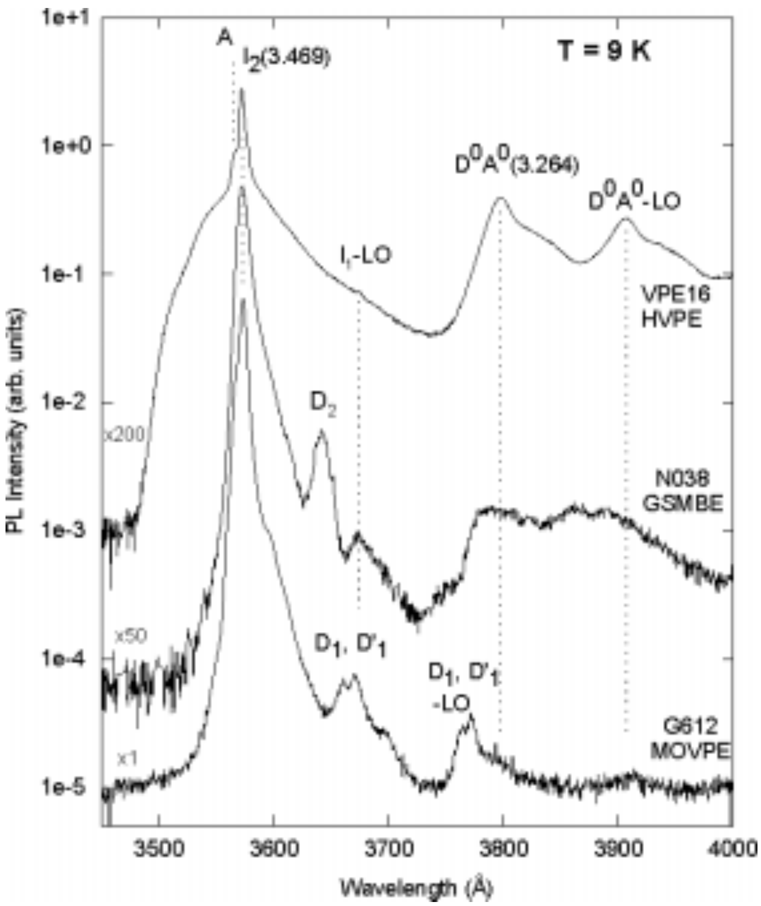

Figure 1. Luminescence spectra (log scale) at 9 K of nominally undoped GaN/Al_2O_3 samples grown by HVPE, GSMBE and MOVPE, from top to bottom.

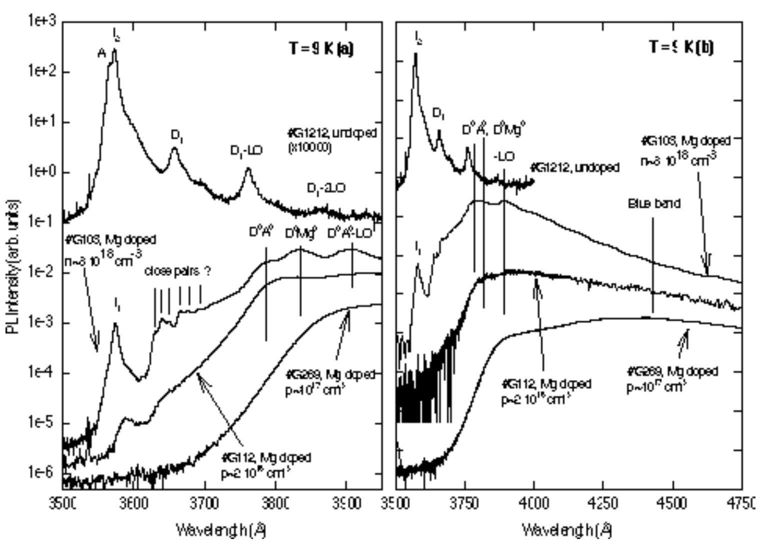

Figure 2. Luminescence spectra at 9 K of undoped and Mg doped MOVPE-grown GaN, with increasing Mg doping levels. (a): near edge transitions. (b): on an expanded energy range.

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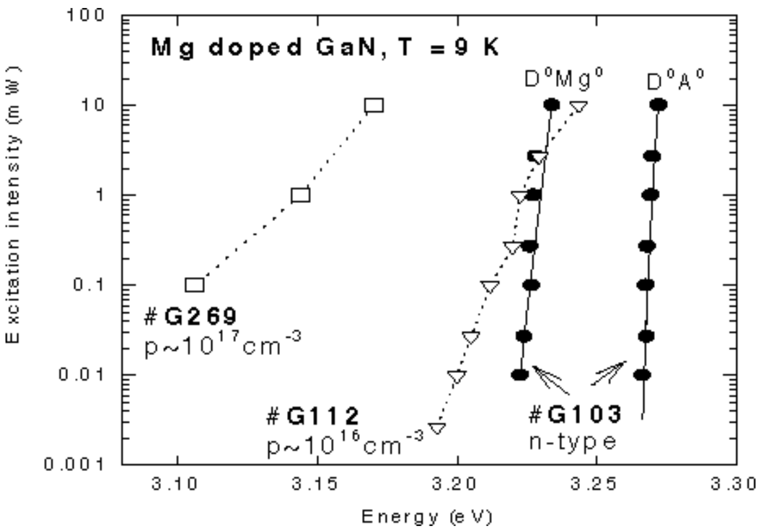

Figure 3. Excitation intensity dependence of the peak energies of donor-acceptor pair bands in Mg doped GaN for various doping levels. Solid lines are a fit according to reference [8]. Dotted lines are guides to the eyes.

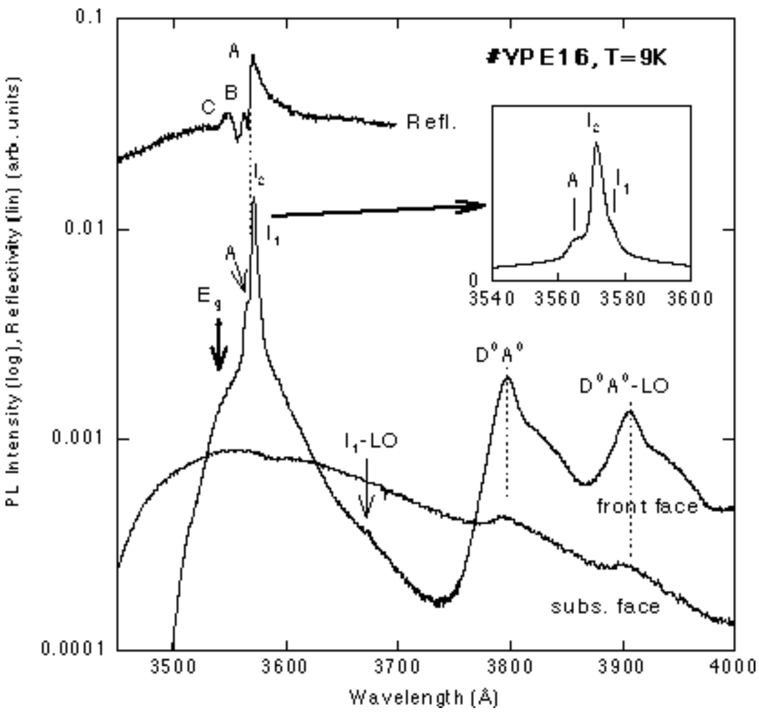

Figure 4. Luminescence and reflectivity spectra at 9 K of a 100 µm thick undoped HVPE grown GaN sample. PL spectra are given recorded from the surface and substrate faces.

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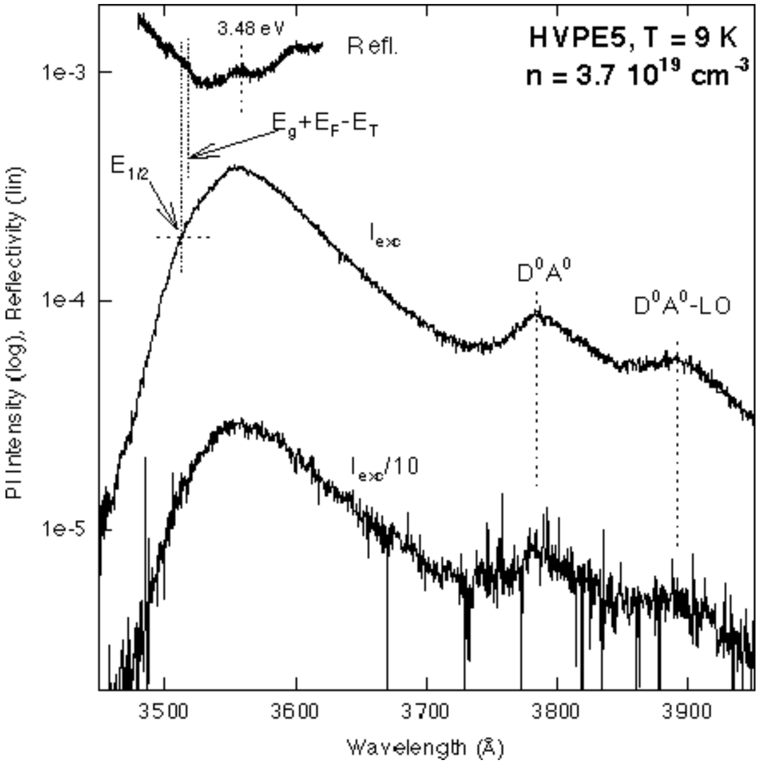

Figure 5. Luminescence and reflectivity spectra (9 K) of an n^+ HVPE grown GaN layer.

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