Photoluminescence and Hall Studies of GaN:Fe and (Ga,Fe)N:Mg Layers

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Temperature dependent photoluminescence (PL) in the ultraviolet regime and Hall measurements at room temperature have been performed on Metal-Organic-Chemical-Vapor-Deposition grown GaN:Fe and (Ga,Fe)N:Mg layers. PL measurements were employed in order to study the dopants' influence on the near-band edge excitonic emission and their tendency to provoke the formation and suppression of defects or incorporation of impurities. For their identification and for the understanding of the PL spectra the evaluation of the free carrier concentrations via Hall measurements was necessary. Depending on the iron concentration of the (Ga,Fe)N layers, the near-band edge emission goes through two different stages: at low Fe-concentration no excitonic emission can be seen whereas with higher doping levels, excitonic features develop. The (Ga,Fe)N films exhibit n-type behavior. The Mg codoped samples show strong Mg and defect related luminescence bands, whose occurrence and intensity also strongly depends on whether high or low Fe concentration is present. The (Ga,Fe)N:Mg layers were semi insulating.

Introduction

Transition metal doped GaN has been predicted theoretically to be an apt candidate for the realization of novel Diluted Magnetic Semiconductors (DMS) for spintronic applications. Employing Zener's model of ferromagnetism, Dietl et al. [1] calculated a Curie temperature TC exceeding room temperature (RT) for p-type Mn doped GaN. These layers have a Mn concentration of 5% and 3.5×10^{20} holes/cm^3, which is necessary for carrier-mediated exchange coupling between localized spins and thus ferromagnetic spin alignment. The localized spins are provided by the transition metal incorporated substitutionally on Ga lattice sites. The Zener type ferromagnetism for GaN:Mn could not be realized due to the presence of a Mn^{3+} level decreasing the free hole concentration [2]. Thus, our research has switched to the promising material system GaN:Fe and (Ga,Fe)N:Mg.

Experiments

Temperature dependent PL in the ultraviolet (UV) regime and Hall measurements at RT have been performed on Metal-Organic-Chemical-Vapor-Deposition (MOCVD) grown GaN:Fe and (Ga,Fe)N:Mg layers. Two different doping procedures have been

employed: bulk and delta doping. In the bulk-doping, the doping precursor-line valve was opened during the whole layer growth. This procedure was employed for the GaN:Fe samples presented in this work. In the case of the delta-doping, the doping elements have been brought into the films layer by layer, separated by a pure GaN intermediate layer of about 25 nm. Thus the growing sequence is …GaN/Fe/GaN/Mg… etc.

PL measurements were employed in order to study the dopants' influence on the near-band edge excitonic emission (NBEE) and their tendency to provoke the formation and suppression of defects or incorporation of impurities. For their identification and for the understanding of the PL spectra the evaluation of the free carrier concentrations via Hall measurements was necessary.

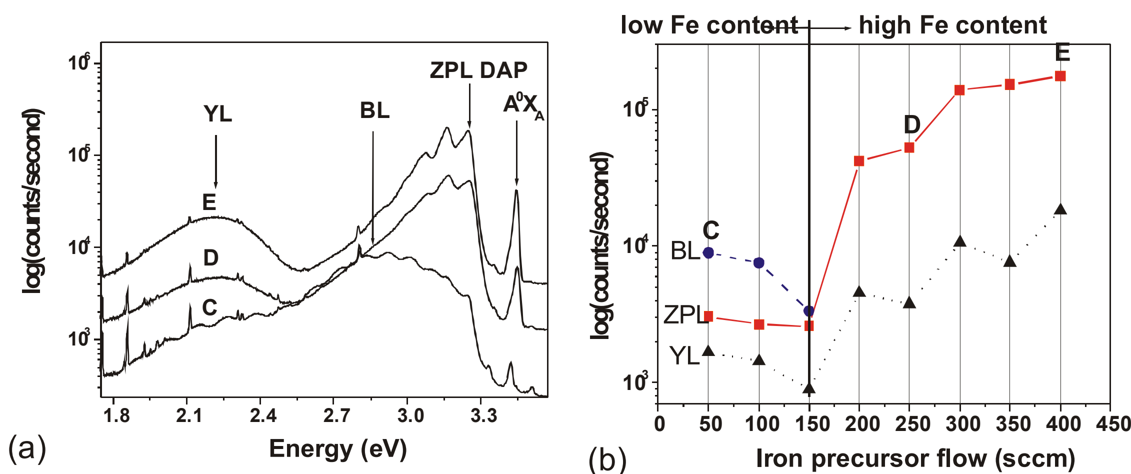

Fig. 1 (a) PL spectrum of samples A and C at 10K. The inset shows the excitonic region of sample C with its donor-bound-exciton (D^0X_A), two-electron-satellite ($D^0X_{A,n=2}$) and phonon replicas of bound (D^0X_A +LO) and free exciton (FX_A+LO). (b) shows in logarithmic scale the evolution of the NBEE as a function of the iron precursor flux for a whole series of samples.

Results and Discussion

1. GaN:Fe:

Sample A was grown with an iron precursor flow of 50 sccm and sample C with a flow of 350 sccm. The spectrum of sample A exhibits a defect-related yellow luminescence (YL) band which centers at 2.2 eV and a second weakly developed blue luminescence band (BL) peaked at 2.8 eV. On the spectrum of the highly iron doped sample C, these bands can be seen as well. In addition, the spectrum exhibits a fairly strong NBEE, whose intensity turned out to scale strongly with the iron precursor flux. Figure 1(b) shows the development of the intensity of the NBEE as a function of the iron content of a whole series of differently doped GaN:Fe samples. At low fluxes, practically no NBEE is formed, whereas between a flux of 150 sccm (sample B) and 350 sccm (sample C) the intensity rises by about three orders of magnitude. The peak broadening of the NBEE is, with a FWHM of 4.65 meV, quite large. It differs from sample to sample only slightly and could not be correlated with the Fe-content. Hall measurements at RT revealed n-type character of these samples and resulted in electron concentrations between 6.7×10^{16} for sample B and 9.1×10^{17} electrons/cm³ for sample C rising with in-

creasing iron flux. The exact origin of the increased electron concentration in the Fe-doped samples compared to the GaN ones is unknown at present due to difficulties in distinguishing between the contributions from nucleation, buffer and doped layer. Comparison of the determined positions and thermal activation energies with PL studies on MOCVD grown nominally undoped GaN [3] allows to attribute the NBEE to a neutral-donor-bound exciton D^0X_A that is related to the upper valence subband of hexagonal GaN. The low intensity emission at 3.4609 eV (see inset in Fig 1(a)) is assigned to a two electron satellite $D^0X_{A,n=2}$, where the dissociation of the D^0X_A leaves the donor in its excited n=2 state [4] – [6]. From the distance of the principal D^0X_A line and the $D^0X_{A,n=2}$ times 4/3 the donor-ionization energy can be obtained. In our case it results in E_D ~ 30 meV and is comparable to the value determined before. The values of E_D point to oxygen or silicon as principal binding site for the D^0X_A [7] as confirmed by an increase in the oxygen and silicon concentration from SIMS data, but interstitially incorporated iron acting as a double donor can not be excluded. The inset in Fig. 1(a) also presents the longitudinal phonon (LO) replica of the D^0X_A and FX_A. The comparison of the intensities of the phonon replica illustrates a weaker phonon coupling of the bound than of the free exciton. From the results presented above, it seems likely that depending on the iron doping level, two types of spectra are measured: with low Fe concentration, the excitonic luminescence measured on nominally undoped GaN reference sample vanishes. The reason could be that due to the introduction of a donor $Fe^{3+/4+}$ and an acceptor $Fe^{2+/3+}$ state [8], the free carriers forming excitons are trapped immediately after excitation. At high doping fluxes the dominating excitonic emission of pure GaN appears again. From AFM, MFM and TEM studies it can be argued that the growth mode is changed when reaching the saturation limit of Fe in GaN [3], [9] leading to regions of pure GaN in the (Ga,Fe)N films. The saturation limit seems to be related to an iron content of about 1– $3x10^{20}$ iron atoms/cm³ corresponding to a precursor flux of 150 sccm. Another explanation is that due to the elevated electron concentration the Fe charge state is shifted towards a higher Fe^{2+}(d6) state resulting in a lower suppression of the exciton formation since the $Fe^{3+/4+}$ donor state can not be active any more.

2. (Ga,Fe)N:Mg:

As mentioned above, the Mg-Fe codoped samples have been grown following a delta-doping procedure at 950 °C. The single iron or magnesium delta layers are separated by about 25 nm of pure GaN. The Mg flux was kept at 350 sccm whereas the iron flux was varied between 50 and 400 sccm. Hall measurements revealed a semi insulating character of this series. Fig. 2(a) shows PL spectra of samples D, E and F at 10 K. The iron fluxes of the three samples were 50, 250 and 400 sccm. The spectra exhibit three luminescence bands, a YL band peaked at 2.2 eV, a blue luminescence band (BL) centered at 2.8 eV and the third band which has its zero-phonon-line (ZPL) at 3.25 eV. The development of the intensities of these three bands over the iron flux is presented in Fig 2(b). The intensities of the YL and the 3.25 eV ZPL emissions rise, whereas the BL quenches with increasing Fe-concentration. The intensity of the 3.25 eV ZPL rises two orders of magnitude between 150 and 400 sccm. The calculation of the activation energy from its thermal behavior leads to a value of 58.6±17.6 meV. The authors of Ref. [10] and Ref. [11], respectively, report on the formation of similar band at 3.27 eV particularly in n-type silicon codoped GaN:Mg and slightly doped GaN:Mg. They assign this emission to a shallow donor-shallow acceptor pair transition, but report on an activation energy of 210 meV and 160 meV attributed to the thermal release of trapped holes from the Mg acceptor state. However, as we can not consider the effect of band-benching and potential-fluctuations introduced by the delta doping procedure at the moment, an interpretation of the measured values remains difficult. The BL intensity lowers with increasing iron content. The free holes of GaN:Mg are most likely compensated with the introduction of iron raising the Fermi level and thus the formation energy [12] of the deep defect-related donor complex that is responsible for the 2.8 eV transi-

tion. The YL band quenches with iron contents between 50 and 150 sccm, followed by a strong increase between 150 and 400 sccm. This is probably due to a change in the defect states leading to the YL due to iron doping to be confirmed by the evaluation of activation energies on low and high Fe doped (Ga,Fe)N:Mg layers from further temperature-dependent PL studies. The narrow emission at 3.445 eV labeled A^0X_A is commonly attributed to an acceptor-bound exciton whose binding sites are Mg acceptors [13].

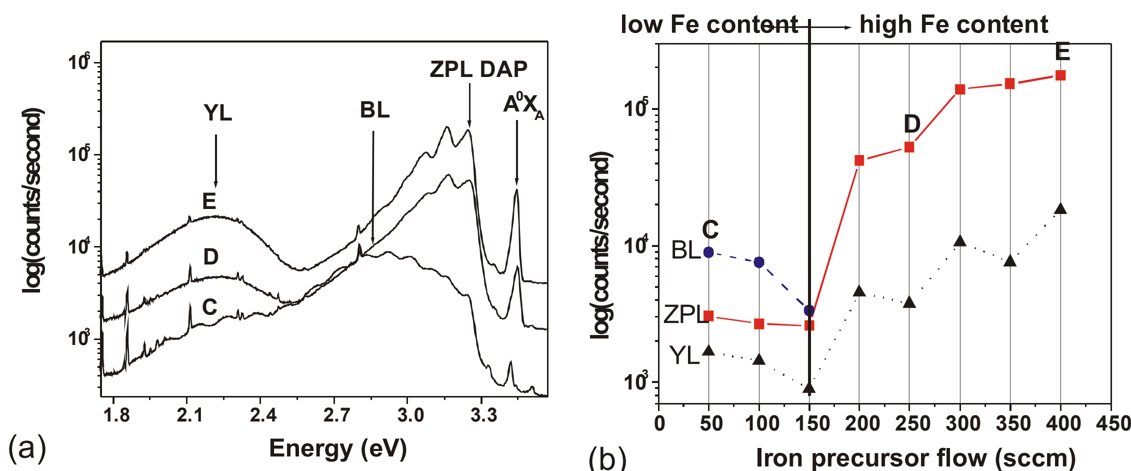

Fig 2: (a) PL spectra of samples D, E and F at 10 K. (b) Evolution of the intensity of the three luminescence bands over iron precursor flux for a whole (Ga;Fe)N:Mg series.

Conclusion

Temperature dependent PL and Hall measurements have been made on MOCVD grown GaN:Fe and delta doped (Ga,Fe)N:Mg samples. The spectra of both material systems exhibit a dependence on the iron precursor flux in the MOCVD process and thus on the overall iron concentration. Different PL transitions can be measured, for high and low iron concentrations. GaN:Fe spectra show a donor-bound exciton whose intensity scales with the iron flux. In contrast, the codoping of Fe and Mg leads to the formation of defect bands, especially to the formation of DAP transition at 3.25 eV as well as an acceptor-bound exciton. In both materials, a threshold for the formation of the iron-related emissions of 150 sccm iron precursor flux can be stated. We attribute this behavior to the saturation concentration of iron on Ga sites, where new, secondary phases are formed and interstitial iron incorporated. Hall measurements reveal n-type behavior of the GaN:Fe layers and a semi insulating character of the codoped samples.

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