TIME RESOLVED PHOTOLUMINESCENCE OF CUBIC MG DOPED GAN

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Abstract

Mg doped cubic GaN layers were studied by steady state and time resolved photoluminescence. The blue emission due to Mg doping can be decomposed in three bands. The decay curves and the spectral shift with time delays indicates donor-acceptor pair behaviour. This can be confirmed by excitation density dependent measurements. Furthermore temperature dependent analysis shows that the three emissions have one impurity in common. We propose that this is an acceptor level related to the Mg incorporation and the three deep donor levels are due to compensation effects.

Introduction

GaN is found to exist in a thermodynamically stable hexagonal and in a metastable cubic phase [1]. Substrates for the cubic material are much easier available, cleavage is less complicated and due to the higher symmetry superior electronic properties are expected. In order to achieve optoelectronic devices based on p-type cubic GaN it is important to study its fundamental properties. As in hexagonal samples, the basic properties like recombination channels of Mg doped cubic GaN samples are still not completely understood. Lightly and moderately doped samples show besides the excitonic transitions at 3.27eV, the donor-acceptor pair DAP transition at 3.15eV and a Mg related DAP recombination at 3.04eV [2]. For heavily doped samples ($[Mg] > 10^{18} \text{ cm}^{-3}$) deep Mg related transitions are observed. In this work these deep blue emissions are studied by steady state (SS) and time resolved (TR) photoluminescence.

Experiment

The cubic GaN layers were grown by plasma-assisted molecular-beam epitaxy on semi-insulating (100) GaAs substrates at a substrate temperature of 720°C. Details of the growth procedure were reported elsewhere [3]. For Mg doping, a commercially available effusion cell with an orifice of 3mm was used. The thickness of the GaN layers varies between 700 and 900nm. Mg concentration and depth distribution was determined by secondary ion mass spectroscopy. In this work samples with Mg concentration from $2.3 \cdot 10^{18}$ to $5 \cdot 10^{18} \text{ cm}^{-3}$ were analysed. Results are compared with an non-intentionally doped (nid) sample.

For steady state (SS) photoluminescence PL measurements we used the 325nm line of a HeCd laser. Excitation intensity was varied by neutral density (ND) filters. Time resolved (TR) measurements were carried out with a pulsed Xe lamp as an excitation source and a boxcar system for detection. The emission was dispersed and detected in both cases by a monochromator (1m, 1200/mm) and a photomultiplier, respectively. The samples were cooled down to 10K by a closed-cycle He cryostat. The temperature could

be varied from 10K to room temperature by a heating resistance. The temperature was measured by a thermocouple.

Results and discussion

Figure 1 shows SSPL spectra of a heavily Mg doped and a nid sample. In the nid layer there is a strong emission at 3.27eV and 3.15eV ascribed to excitonic and pair emission, respectively. In the heavily Mg doped samples the PL spectra are dominated by a broad blue band composed of three emissions. The 3.27eV and 3.15eV emissions are hardly detectable in these layers.

Fig. 1: Low temperature (10K) SSPL spectra of Mg doped and undoped GaN sample

The exciton recombination at 3.27eV and the DAP emission at 3.15eV are quenched and recombination takes place at lower energies. Doping cubic GaN layers with Mg introduces alternative recombination channels.

The comparison of SS and TR spectra shows a shift to lower energies in TR spectra (figure 2). Furthermore the low energy side of the emission is less quenched than the high energy side. This is an indication for an energy dependent transition probability. For a quantitative analysis the SS and TR spectra for various time delays were fitted to three Gaussian curves. In the SSPL spectrum the three Gaussians are peaked at 2.968eV (FWHM: 173meV), 2.789eV (FWHM: 239meV) and 2.512eV (FWHM: 318meV). The energetic distance between the three bands were maintained when fitting the spectra. The three bands shift to lower energies with increasing time delay (TD). The maximal shift (79meV) is reached at a TD of 10ms. Further increase of the TD does not result in a further shift. The shift to lower energies is accompanied by a very small narrowing of the

bands. The energetic distance between the three bands could be maintained which means that all three bands show the same shift.

Decay curves were determined at various energies of the spectrum (figure 3). They all follow a power law $I(t) \sim t^{-a}$ rather than exponential decays. The exponent a is increasing from 1.00 to 1.43 with increasing energy position. This is a sign for slower emission at the low energy side. This behaviour is typical for distant DAP recombination.

Fig. 2: SS and TR PL spectra of a heavily doped GaN:Mg sample

Fig. 3: Decay curves at various energies.

The recombination energy of a DAP is [4]:

$$h\nu = E_g - (E_A + E_D) + e^2 / 4\pi\epsilon_0\epsilon R \quad (1)$$

where E_D and E_A are the donor and acceptor ionisation energies and R is the distance between the donor and the acceptor. The recombination energy decreases with the distance between the impurities and so does the overlap of their wavefunctions. Therefore the recombination probability is lower for more distant pairs and thus the decay time is longer. Calculating the exact decay curves is rather complicated but it has been shown [5] that the decay follows approximately a power law with exponents between 1 and 2.

In figure 4 the spectra are shown for 3 different excitation intensities. With higher excitation intensity the whole band shifts to higher energies and the high energy side increases in intensity. The shift rate amounts approximately to 7meV per decade of excitation intensity. The increase of emission intensity with excitation density follows a power law:

C_1 and C_2 are two temperature independent constants and k_B is the Boltzmann constant. All three bands show a similar behaviour with $E_{a1} \sim 50\text{meV}$ in all cases and E_{a2} varying between 4 and 6meV. This indicates two quenching processes for all three bands. The activation energy of 50meV cannot be directly related to any energy level of impurities mentioned in literature. However the activation energy is not in all cases equal to the localisation of the impurity within the band gap. Only if the thermal release of the carriers is the rate-limited process one can assume $E_a = E_{D/A}$ [5]. If a thermal equilibrium process is rate-limited process E_a is less (often: $E_{D/A}/2$). In this case E_{a1} could be related to a donor level of 160meV determined via Hall-measurments in n-d layers [9].

Since the second activation energy is very small, it might be attributed to a

Fig. 6: SSPL spectra for various temperatures

Fig. 7: PL intensity of the three bands as a function of

temperature dependence of the capture cross-sections [5].

We expect that substituting Ga for Mg introduces an acceptor level in the material. Therefore we propose the following model. The three bands can be described by recombinations between a hole trapped at a relatively shallow acceptor level ($\sim 200\text{meV}$ [2]) due to Mg on the Ga site and electrons trapped at three donor levels related to compensation effects due to the incorporation of Mg in the material. Such a compensation mechanism was already found in hexagonal GaN [10]. The three bands are very broad, structureless and show an almost perfect Gaussian lineshape. DAP no-phonon emissions are instead much narrower and normally show an asymmetric lineshape because of the broadening due to the Coulomb term. Therefore we suppose that the three bands are an overlap of the zero phonon lines (ZPL) with the phonon assisted

transitions of DAPs rather than only zero-phonon transitions. The condition for this, a strong phonon coupling is very probable in a polar material like GaN. A similar situation was reported in hexagonal GaN:Mg [8]. The Franck-Condon shift was estimated by assuming a coupling to merely 90meV phonons in order to determine the exact position impurity levels within the band gap. Since we do not know at the moment which phonons are involved any assumption of the levels would be a mere speculation. We think of a coupling to low energy phonons because the emissions are completely structureless. Coupling to 90meV phonons would lead to structured emissions and furthermore would we expect an intensity distribution as in the case of the 3.15eV pair in the n-d sample, e.g. the ZPL should have a higher intensity than the replicas. The situation could be even more complicated because we cannot exclude non-linear phonon coupling.

Conclusions

We studied cubic GaN samples heavily doped with Mg. The results of SS and TRPL measurements depending on excitation density and temperature are all consistent with three DAP emissions having one common impurity. Therefore we suppose that Mg doping introduces besides an acceptor level also three deep donor levels due to compensation effects in the material.

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