

Defects in Cubic and Hexagonal GaN Epilayers

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We report a comprehensive photoluminescence investigation of defects in hexagonal GaN crystals deposited on Al₂O₃ and 6H-SiC substrates and of cubic GaN deposited on GaAs. Intensive free and bound exciton luminescence was observed for the bulk hydride vapor phase epitaxy GaN layers. Dislocation bound excitons at 3.36eV and 3.31eV are observed at the GaN/Al₂O₃-interface and in the GaN/SiC samples. The exciton of the cubic GaN is found at 3.262eV. The broad 2.4eV luminescence was mainly detected in the interface region between the GaN layer and the sapphire substrate. Transition metal incorporation results in a decrease of the near-band-gap emission intensity and gives rise to structured 3d luminescence bands in the near infrared spectral region.

1. Introduction

The InGaAlN alloy system is very promising for applications as widegap LEDs and injection lasers, as well as for high-temperature electronics. Up to now, extensive investigations have been performed on samples with wurtzite symmetry, but some groups are even able to prepare zincblende-structure layers on various substrates. For cubic GaN the situation is such that even the precise band gap energy is still a matter of controversy [1,2]. An unambiguous distinction between the cubic and hexagonal phase domains can be achieved by Raman spectroscopy [3] and x-ray spectroscopy [4]. The investigation of impurity, native point or extended defect properties is essential to optimize the device quality. Consequently, there is strong interest in defect-related properties of GaN in the hexagonal and cubic modification. Up to now, only very few comparative defect studies for both modifications exist. We investigated the optical properties of hexagonal and cubic GaN epilayers by means of photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy. PL spectra are taken from the band-gap region down to the near-infrared spectral region. The aim of this paper is to give a comprehensive overview about the luminescence properties of different GaN crystals.

2. Experimental

We investigated hexagonal GaN layers deposited on sapphire and SiC substrates. The hexagonal bulk-like samples with thickness between 220µm and 400µm were grown by hydride vapor phase epitaxy (HVPE) [5]. The hexagonal GaN samples on 6H-SiC were grown by means of high temperature vapor phase epitaxy (HTVPE) [6] or by a modification of the sandwich technique [7]. Cubic GaN samples were grown on (001) GaAs by molecular beam epitaxy (MBE). Reflection x-ray diffraction

spectra taken from these samples show only cubic diffraction peaks indicating that the plane perpendicular to the x-ray scan did not contain hexagonal GaN lattice planes. The phase purity of the cubic samples was also checked by Raman-spectroscopy. We obtain a 1% contribution of hexagonal subdomains in the cubic samples.

3. Results

Excitonic and DAP Recombinations

The spectral range between 3.26eV and 3.50eV is usually dominated by the recombination of free and bound excitons. Figure 1A represents a typical spectrum of a n-conducting HVPE sample grown on Al₂O₃. Sample A is a 400μm thick HVPE sample without buffer layer. The donor-bound-exciton line I₂ at 3.4728eV is most prominent. Emission from the free A-exciton is seen at 3.4800eV [8]. The localization energy of the exciton thus amounts to 7.2meV. High resolution spectra reveal the presence of a weak second donor-bound-exciton line with a localization energy of 3.6meV. The FWHM of the I₂ amounts to 920μeV, a value that confirms the high quality of HVPE-grown bulk GaN and its potential for a lattice-matched substrate material. Sample B is a GaN/SiC sample grown by the sandwich technique. In contrast to the high quality HVPE samples no strong I₂ and free exciton recombination are observed. Two emissions peaking at 3.366eV and 3.311eV are also observed. Spectra like this are typical for disturbed GaN. The decay time of the I₂ line at 1.8K in the HVPE sample is 70ps [9] whereas 35ps are obtained in the GaN/SiC samples. The luminescence transients between 3.36eV and 3.31eV reveal a monoexponential decay with time constants between 45ps and 600ps [10]. On the basis of this monoexponential decay, donor-acceptor-pair recombination as suggested [11] for the 3.311eV line can be excluded as interpretation of this luminescence. Instead, we attribute these lines to excitonic recombination at dislocations. Dislocation excitons are well known in other materials like CdS [12]. In the PL spectra of the cubic GaN sample (C) the 3.366eV and 3.311eV emission lines are also observed. Additionally, a luminescence peaking at 3.262eV is detected. Due to the fact that the bandgap of the cubic modification is estimated at about 3.28eV [2], a shift of the exciton emissions of about 0.2eV is expected. We observe a shift of about 0.211eV and thus the 3.262eV luminescence can be attributed to the bound exciton of the cubic modification, whereas the other two luminescence lines are interpreted as luminescence from disturbed hexagonal subdomains. For the donor-acceptor pair recombination we observe only a shift of about 0.131eV between sample A and C, indicating the presence of more shallow impurities in the cubic GaN.

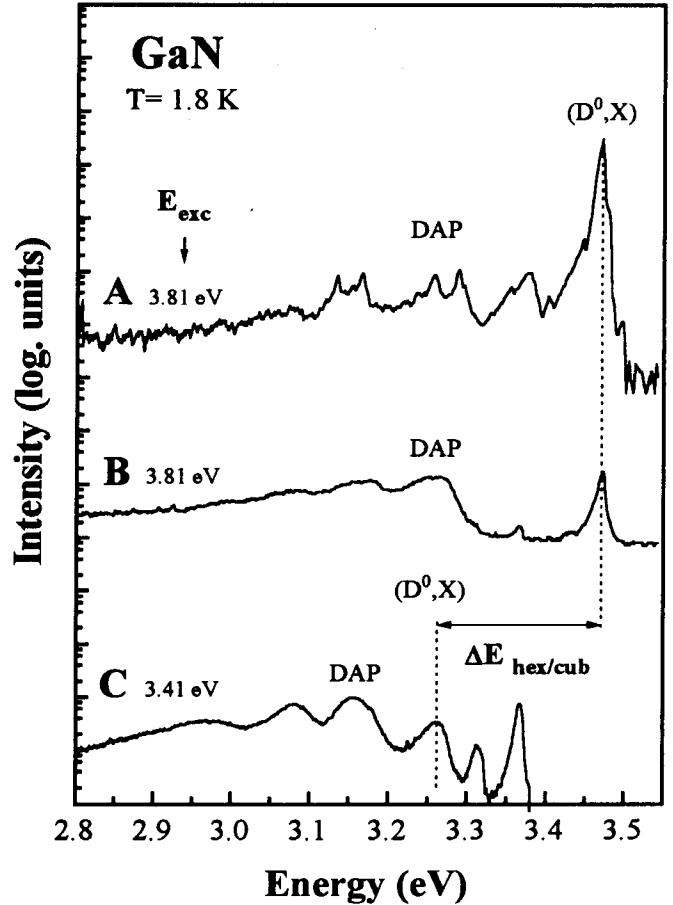


Fig. 1: PL-spectra of hexagonal GaN/Al₂O₃ (A), GaN/6H-SiC (B) and cubic GaN/GaAs (C). Sample A and B are excited at 3.81eV, sample C is excited at 3.41eV. The energy difference between the hexagonal and the cubic excitons is indicated.

Deep-Level Recombinations

There has been much effort aimed at doping GaN p type by introducing group II and IV elements. Generally, most of these dopants reveal a broad luminescence peaking between 3.2eV and 2.2eV [13]. They are interpreted in terms of recombination with at least one deep acceptor or donor involved. The sample A exhibits a broad luminescence band peaking at 2.4eV (Fig. 2). At room temperature the luminescence intensity of this band exceeds that of the excitonic recombination. Similar luminescence bands are also known from several II-VI semiconductors like ZnS.

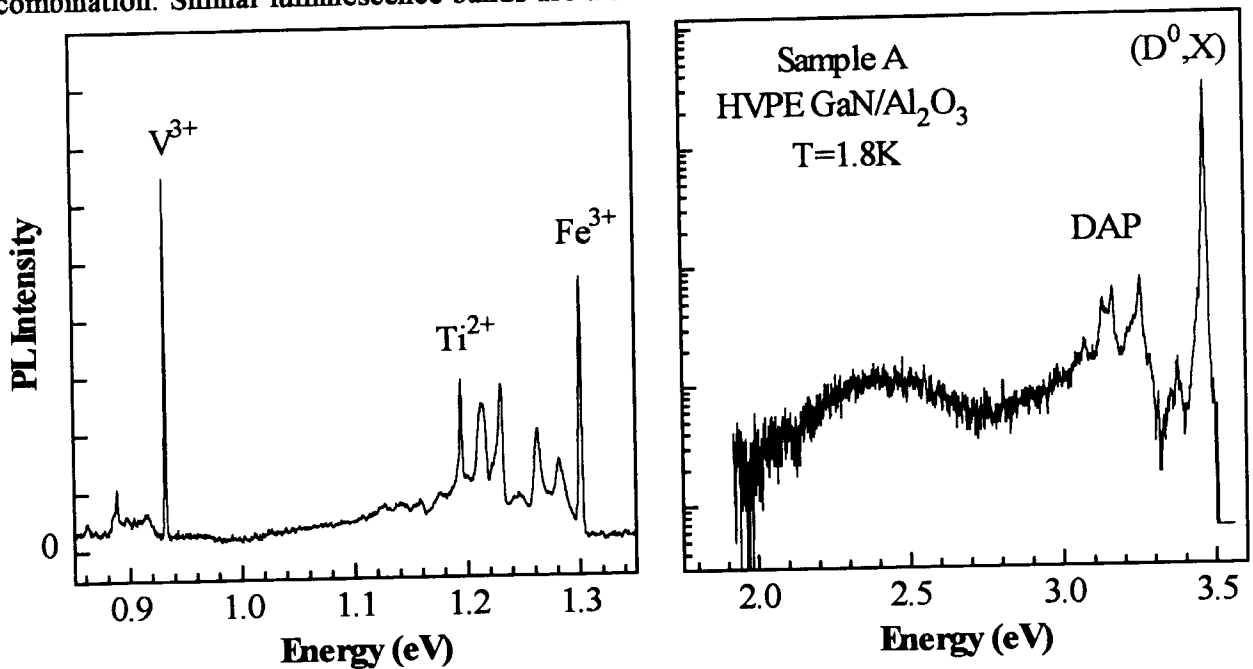


Fig. 2: PL-spectra of the hexagonal GaN HVPE sample A at 1.8K. The crystal is excited at 3.81eV (right Fig.) and at 2.6eV (left Fig). The 2.4eV luminescence originates mainly from the interface region.

They are often interpreted as a recombination between shallow donors and deep acceptors in which the donors or acceptors are built by anion or cation vacancies and the corresponding dopant. The creation of intrinsic vacancies is very probable near surfaces, interfaces or grain boundaries. In order to clarify whether the 2.4eV luminescence is an intrinsic property of GaN or caused by defects located near the interface to the substrate, we performed spatially-resolved PL and Raman-measurements on hexagonal GaN/ Al_2O_3 samples. Our investigations reveal that the photoluminescence originates mainly from both the substrate interface and a region of structured reorientation near the interface where the c-axis of the GaN layer rotates by 90° from a direction parallel into a direction perpendicular to the substrate interface. This is verified by Raman-spectroscopy in combination with the observed Raman-peaks and the selection rules [14,15]. This luminescence band is only detected in the hexagonal HVPE GaN sample A. Additionally, it is inhomogeneously distributed in the interface region. One of the most prominent native defects in GaN is the nitrogen vacancy, sometimes attributed to cause the n-type conductivity [16]. It is also suggested that the yellow luminescence at 2.2eV is connected with the nitrogen vacancy [17]. However, the discussion is still controversial, but our results demonstrate the importance of the disturbed interface for the 2.4eV luminescence process. None of these broad luminescence bands can be detected in the cubic MBE GaN samples.

Transition Metal Recombinations

The spectral range between 0.7eV and 1.4eV is dominated by the intracenter recombination of transition metal (TM) elements (Fig. 2). The TM impurities act as minority lifetime killers and open up additional nonradiative recombination channels for excited electrons and holes leading to a decrease of the near-band-gap emission intensity. In the older GaN/SiC and GaN/ Al_2O_3 samples transition metals are incorporated as natural contaminations during growth. As yet, four TM related luminescence bands are

observed. On the basis of Zeeman and ODMR measurements the 1.3eV luminescence is unambiguously assigned to the Fe^{3+} (${}^4\text{T}_1\text{-}{}^6\text{A}_1$) transition [18,19], whereas the origin of the other three luminescence bands is still controversial. In order to clarify their chemical origin we investigated TM codoped GaN layers grown on 6H SiC. The 1.19eV luminescence has been attributed to the ${}^1\text{E-}{}^3\text{A}_2$ transition of either Cr^{4+} [20] or Ti^{2+} [21]. We observe the luminescence only in the Ti doped crystals whereas no signal could be detected in the Cr doped sample. For the remaining two luminescence bands no codoping influence is observed and the assignment to $\text{Co}^{2+}/\text{Ni}^{3+}$ (1.047eV) and V^{3+} (0.931eV) remains tentative. Fe and Ti were the most common TM contaminations because they are observed in several GaN-samples. The onsets of the Fe^{3+} PLE-spectra in GaN/ Al_2O_3 and AlN were used for the determination of the band offsets according to the internal reference rule of Langer and Heinrich [22]. Band discontinuities are very important parameters for the characterization of the heterostructures. Our PLE spectra are partly different to these, published by Baur et al [23]. They locate the $\text{Fe}^{2+/3+}$ acceptor level in GaN 2.5eV above the valence band. However, our PLE-spectra of Fe^{3+} are dependent on the sample and thus the reported band offsets are questionable. We investigated the Fe^{3+} PLE in n-type HVPE GaN samples and semiinsulating GaN/SiC samples. For the semi-insulating GaN we were able to detect higher lying Fe^{3+} levels at 2.02eV and 2.728eV. Additionally, a (Fe^{3+} , e,h)-complex could be detected at 2.814eV. However, details of these spectra are beyond the scope of this paper and will be published separately [24], but the results explain the different excitation behavior of Fe^{3+} in semi-insulating and n-type GaN mentioned above.

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