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Optical Properties of Carbon Doped Cubic GaN Epilayers Grown on GaAs (001) Substrate by Molecular Beam Epitaxy

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ABSTRACT

The optical properties of Carbon doped cubic GaN epilayers have been investigated by temperature and intensity dependent photoluminescence measurements. RF-plasma assisted molecular beam epitaxy equipped with an e-beam-evaporation source for carbon doping is used to grow the cubic GaN layers on GaAs (001) substrates. With increasing Carbon flux a new photoluminescence line at 3.08 eV appeared at 2K. This line is attributed to a donor acceptor transistion, which involves the shallow C_N acceptor. From the spectral position the binding energy of the C acceptor is estimated to be about $E_C = 0.215$ eV. Our experiments demonstrate that C indeed introduces a shallow acceptor in cubic GaN with an acceptor binding energy, which is about 15 meV lower than that observed for the Mg acceptor in cubic GaN. However, at high C fluxes a deep red luminescence band appeared at 2.1 eV, indicating compensation effects.

INTRODUCTION

For advanced optoelectronic and electronic devices, like light emitting diodes (LEDs), or laser diodes (LDs) controlled p-type doping and high hole conductivity is crucial [1]. Up to now, Magnesium is used as standard dopant in Molecular Beam Epitaxy (MBE) as well as Metalorganic Vapor Phase Epitaxy (MOVPE). However, Magnesium has several disadvantages which limit the usually reported doping efficiency of Mg in GaN to maximum hole concentrations in the upper $10^{17}cm^{-3}$. This is mainly ascribed to large acceptor ionization energy and compensation effects [2]. MBE-growth further showed that Mg is very volatile, requires low substrate temperatures and N-rich growth conditions [3,4]. These conditions are disadvantageous for high quality epilayers, especially for the cubic phase, where N-rich conditions deteriorate phase purity [5].

Among possible alternative acceptor dopants especially Carbon has received a considerable interest due to its similarity to nitrogen in atomic radius and electronegativity. In previous reports, Carbon doping of hexagonal Gallium Nitride (h–GaN) led to semi–insulating properties or to a reduction in background electron concentration [7-9]. In cubic GaN Abernathy et al. [10] reported on p-type doping by carbon. However, due to the use of CCl_4 a pronounced reduction in growth rate prohibited the incorporation of higher C concentrations and the maximum hole concentration reached was 3×10^{17} cm^{-3}.

In this contribution we report on the optical properties of carbon doped cubic GaN epilayers. Carbon doping has been performed by rf-plasma assisted molecular beam epitaxy using an e-beam evaporation source. Our experiments clearly demonstrate that C indeed introduces a shallow acceptor in cubic GaN with an acceptor binding energy, which is about 15 meV lower than that observed for the Mg in c-GaN.

EXPERIMENTAL

Cubic GaN (c-GaN) was grown by rf-plasma assisted molecular beam epitaxy (MBE) on semi-insulating GaAs (001) substrates [5]. C-doping of c-GaN was achieved by e-beam evaporation of a graphite rod through adjusting the e-beam power between 0 and 400 W. The C-flux was externally calibrated through the growth of C-doped GaAs epilayers assuming the same sticking coefficient for both GaAs and c-GaN and measuring the hole concentration and hole mobility by Hall-effect measurements at room temperature. The knowledge of both mobility and concentration allowed to estimate the compensation and acceptor concentration [11,12]. From results of GaAs:C, it followed that a maximum C-concentration of about 10^{20} cm^{-3} should be achievable in c-GaN.

Secondary ion mass spectroscopy (SIMS) measurements of a C-doped cubic GaN sample, where C was evaporated with the maximum e-beam evaporation power of 400 W indeed showed a C incorporation of 2×10^{20} cm^{-3}. Room temperature Hall-effect measurements of the C-doped cubic GaN epilayers gave hole concentrations and mobilities as high as $6 \times 10^{17} cm^{-3}$ and 200 cm^2/Vs, respectively [6].

Temperature and excitation intensity dependent photoluminescence (PL) measurements were performed in a He bath cryostat between 2 K and 300 K. The luminescence was excited by a 3 mW cw HeCd UV laser and measured in a standard PL system [13]. Neutral density filters allowed a variation of the excitation power over four orders of magnitude.

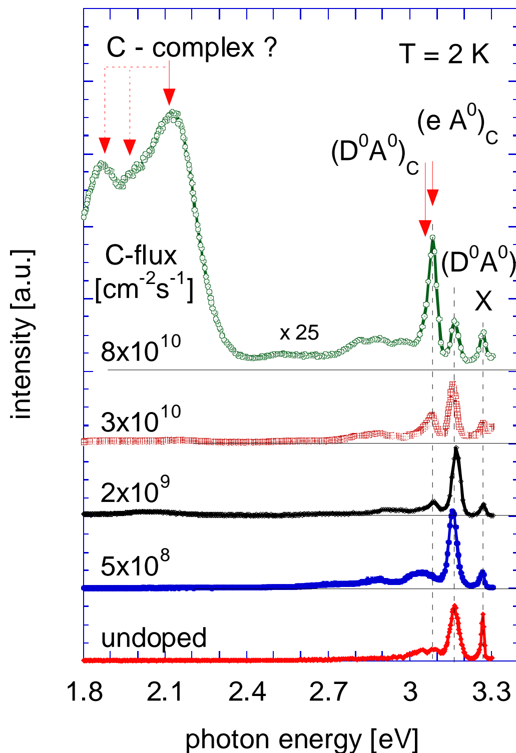

***Figure 1**. Photoluminescence spectra of Carbon doped GaN layers at different e-beam evaporation power. The topmost spectrum has been multiplied by a factor of 25.*

RESULTS AND DISCUSSION

The incorporation of Carbon in cubic GaN has a profound influence on the photoluminescence spectra, as can be seen in figure 1. At low Carbon fluxes, a PL band at E = 3.08 eV appears in the spectra recorded at T = 2 K. This transition is clearly different from the well–known lines X at 3.27 eV and (D^0, A^0) at 3.16 eV, which are commonly seen in cubic GaN [13]. A more detailed analysis of the 3.08 eV band shows, that it is a convolution of two distinct lines separated by 25 meV at low temperatures (indicated by arrows in figure 1). At temperatures above 100 K the low–energy contribution thermalizes and only the high–energy PL transition can be observed. Therefore, we attribute the lower transition to a donor–acceptor recombination $(D^0, A^0)_C$ and the other to a C–related band–acceptor recombination $(e,A^0)_C$, respectively. The

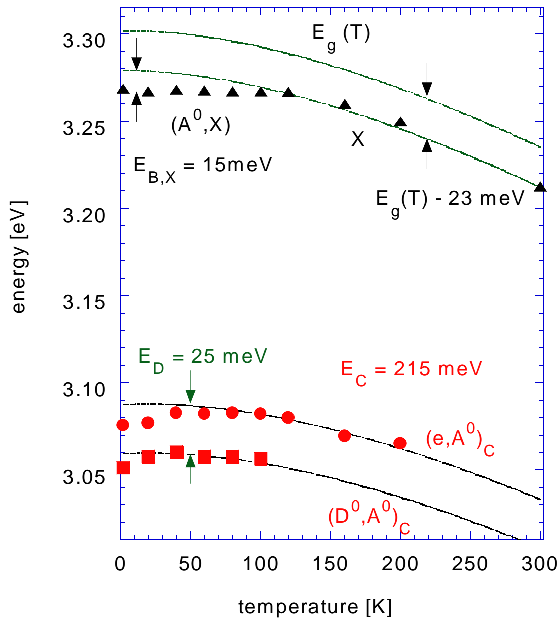

Figure 2*. Temperature shift of the near–band edge PL transitions (trianles: excitonic transition; circles: C–related band–acceptor transition, $(e,A^0)_C$; squares: C–related donor–acceptor transition, $(D^0,A^0)_C$). The top curve shows the gap energy as function of temperature, the lower curves are calculated for $(e,A^0)_C$ and $(D^0,A^0)_C$ transitions, respectively.*

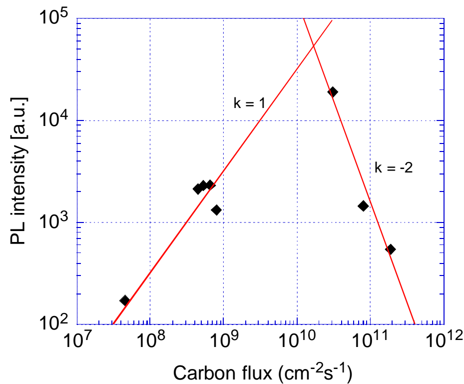

Figure 3*. Low temperature PL intensity of C–related donor–acceptor transition (squares) as function of Carbon flux. The lines with slopes k=1 and k=-2 are guides to the eye.*

energetic positions of the different transitions are shown in figure 2 as a function of temperature. Detailed line shape analysis by fitting the transition at 3.08 eV with two Gaussians yielded an acceptor activation energy of $E_A = 215$ meV. This value is 15 meV below that of the Mg acceptor in c–GaN [14] and is also below the values known for hexagonal GaN:C [15]. The donor involved has the same ionisation energy (25 meV) as the one observed in the undoped samples [13]. The temperature variation of the band gap as measured by photoreflectance [16] is depicted by the topmost full curve.

At moderate Carbon concentrations the integrated intensity of the 3.08 eV band increases linearly with the Carbon flux as indicated in figure 3. This is in agreement with the assumption that the intensity of an donor acceptor band is proportional to the amount of acceptors involved in it [17].

However, above a C-flux of 10^{10} $cm^{-2}s^{-1}$ a clear decrease of the carbon related donor acceptor band intensity is seen. This indicates that at high C-concentration additional deep compensating centers are introduced bypassing the recombination via the shallow carbon acceptor transition. This idea is supported by the appearance of a deep red luminescence at 2.1 eV in the topmost spectra of figure 1.

Two possibilities may be responsible for the strong decrease in the intensity of the carbon related donor acceptor transition. First at high concentrations C atoms may form complexes, which further more do not act as acceptors. This will reduce the number of shallow C acceptors involved in the transition and will decrease its intensity. Second the formation of a deep defect either by C-complex formation or by the introduction of deep intrinsic defects may decrease the internal quantum efficiency and quench the acceptor related PL, too. However, for a quantitative description of this intensity variation a rate equation model taking into account both the near band edge and the deep

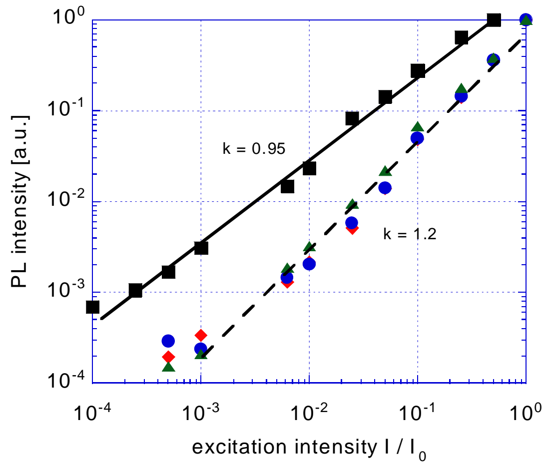

Figure 4. *Photoluminescence intensity of GaN:C as a function of excitation intensity. Diamonds, dots and triangles denote the near–edge luminescence, the squares mark the deep luminescence (C-flux $8x10^{10}cm^{-2}s^{-1}$).*

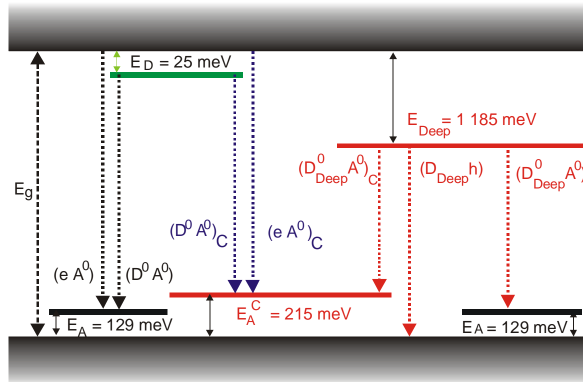

Figure 5. *Schematic diagram of the energy levels in carbon doped cubic GaN epilayers.*

emission will be nessecary.

The localized character of the deep red luminescence at 2.1 eV is further confirmed by intensity dependent PL measurements. Figure 4 shows the intensity increase of both the near band edge transitions and the 2.1 eV emission by varying the excitation intensity at T=2 K. As expected for strongly localized states the slope k in this logarithmic plot is below 1 for a deep level emission (full squares) and is higher than 1 for delocalized states as typically involved in the near band gap emissions (diamonds, triangles and dots, respectively) [18]. In our case the near band edge emissions can be described by a power law $I \sim L^{1.2}$, and the deep luminescence by $I \sim L^{0.95}$, respectively.

Detailed analysis of the red luminescence at 2.1 eV reveal that this band is also convoluted by at least three different transitions, indicated by the full and dashed arrows in the topmost spectrum in figure 1. The energy differences between the main peak and the two low energy peaks correspond nearly exactly to the binding energies of the omnipresent shallow acceptor (E_A = 129 meV) and to the binding energy of the shallow carbon acceptor (E_A^C = 215 meV), respectively. Therefore, we attribute the red luminescence to a superposition of three transitions involving the same deep defect level E_{Deep} located 1.185 eV below the conduction band. Since recently published electrical measurements on our C-doped cubic GaN samples showed also a clear reduction of the free hole concentration at C-fluxes above $8x10^{10}cm^{-2}s^{-1}$ the deep defect must act as a deep donor [19]. The resulting energy diagram is schematically depicted in figure 5.

The nature of the deep compensating complex is unclear up to now. Kaufmann et al. [2] observed similar phenomenons for Magnesium doped MOVPE GaN layers and proposed a self–compensation model via the formation of nearest neighbor $Mg_{Ga}V_N$ pairs. However, C is placed on a N site and the formation of a comparable defect C_NV_N, which is a second nearest neighbor pair, is unlikely. For cubic GaN:C, it is more tempting to apply an analogy to C doped GaAs. In GaAs the formation of a compensating dicarbon split-interstitial center is observed at high carbon concentrations [20]. This complex involves one C atom on a As lattice site and another C atom shifted along the [100] direction [21], and acts as a double donor in GaAs. An equivalent defect in cubic GaN would also explain the slope of k = -2 in figure 3 which implies that at least two Carbon atoms have to be involved in the newly formed deep C-complex.

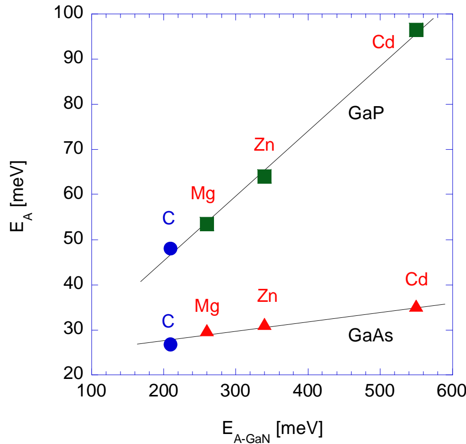

Figure 6. *Acceptor binding energies of C, Mg, Zn and Cd measured in GaP and GaAs versus the corresponding acceptor binding energies in cubic GaN. The lines are guides for the eye.*

Based on effective-mass-theory (EMT) the binding energy of the shallow acceptor can be determined by

$$E_A = \frac{13.58 eV}{\varepsilon(0)^2} \cdot m_{hh} \cdot \gamma \qquad (1)$$

where ε (0) is the static dielectric constant, m_{hh} is the heavy hole mass and γ is a correction factor which depends on the ratio of the light hole to heavy hole mass [22, 15]. Using light hole and heavy hole masses of 0.18 m_0 and 0.75 m_0 for cubic GaN, the correction factor γ is 0.6 [22]. In EMT typically ε (0) is used. However, as pointed out by Orton [23] this should not hold for GaN, where the acceptor binding energies are comparable or even larger than the optical phonon frequencies. In cubic GaN LO and TO phonon frequencies are 92 meV and 67 meV, respectively [24]. In this case it should be more appropriate to use the high frequency dielectric constant ε (∞). Applying ε (∞) = 5.35 we obtain an acceptor binding energy E_A = 0.213 eV which is in excellent agreement with our experimental results and demonstrates that C indeed introduces a shallow acceptor in c-GaN.

In other cubic III-V compounds like GaAs, InP and GaP Carbon is the acceptor with the smallest central cell correction. The binding energy is usually close to Mg and increases in the sequence C, Mg, Zn and Cd [15]. The same sequence is verified now also in cubic GaN as demonstrated in Figure 6, where the acceptor binding energies of C, Mg, Zn and Cd measured in GaAs and GaP is plotted versus the binding energies measured in GaN. As clearly can be seen the binding energy of C is lower than that observed for the Mg acceptor in c-GaN by 15 meV [14]. In addition, due to the higher crystal symmetry, the binding energy of the C acceptor in the cubic phase is also lower than the activation energy of C measured in hexagonal GaN [15].

CONCLUSION

The optical properties of Carbon doped cubic GaN epilayers have been investigated by temperature and intensity dependent photoluminescence measurements. Two new C-related features appears with increasing C concentration. The line at 3.08 eV showed thermalization above 100 K, which is typical for a donor acceptor (D^0A^0) transition involving the shallow C_N acceptor with an activation energy E_A=215 meV. This activation energy is about 15 meV lower than that observed for the Mg in c-GaN. Our experiments demonstrate that C indeed introduces a shallow acceptor in cubic GaN. At an C-flux above $8 \times 10^{10} cm^{-2} s^{-1}$ a deep red luminescence band appeared at 2.1 eV indicating compensation effects. This deep defect lies 1.18 eV below the conduction band.

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