# Electrical and Optical Properties of Carbon Doped Cubic GaN Epilayers Grown Under Extreme Ga Excess

D. J. As, D.G. Pacheco-Salazar[*], S. Potthast, and K. Lischka,
University of Paderborn, Faculty of Science, Department of Physics, Warburger Strasse 100,
D-33095 Paderborn, Germany, d.as@uni-paderborn.de

## ABSTRACT

P-type doping of cubic GaN by carbon is reported with maximum hole concentration of $6.1 \times 10^{18} \text{cm}^{-3}$ and hole mobility of 23.5 $\text{cm}^2/\text{Vs}$ at room temperature, respectively. The cubic GaN:C was grown by rf-plasma assisted molecular beam epitaxy (MBE) under Ga-rich growth conditions on a semiinsulating GaAs (001) substrate (3 inches wafer). E-beam evaporation of a graphite rode with an C-flux of $1 \times 10^{12} \text{cm}^{-2}\text{s}^{-1}$ was used for C-doping of the c-GaN. Optical microscopy, Hall-effect measurements and photoluminescence were performed to investigate the morphological, electrical and optical properties of cubic GaN:C. Under Ga-rich growth conditions most part of the carbon atoms were incorporated substitutially on N-site giving p-type conductivity. Our results verify that effective p-type doping of c-GaN can be achieved under extrem Ga excess.

## INTRODUCTION

Among possible alternative acceptor dopants in GaN especially carbon has received considerable interest due to its similarity to nitrogen in atomic radius and electronegativity [1-3]. Previous experiments by Abernathy et al. [1] showed p-type doping of GaN by carbon grown by metal organic molecular beam epitaxy (MOMBE) on GaAs substrates. 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 $3 \times 10^{17} \text{cm}^{-3}$. Armitage et al. [4] demonstrated that the reduced growth rate could be compensated by suppling high Ga fluxes, however no higher hole concentrations was achieved.

Recently, we have shown that C is indeed the most shallow acceptor in cubic GaN with a binding energy of about 215 meV [5]. Unfortunately due to self-compensation effects the hole concentration saturated and then decreased with increasing C-flux under stoichiometrical growth conditions. A $C_I$-$C_N$ complex is most likely responsible for the observed compensation [6]. To avoid the formation of this complex Ga-rich growth conditions are proposed to increase the incorporation of C at the N substitutional site [7].

In this contribution we report in detail on the incorporation of C in cubic GaN under extrem Ga-rich growth conditions. Optical microscopy, Hall-effect measurements and temperature dependent photoluminescence (PL) are used for characterization. A record hole concentration and hole mobility as high as $6.1 \times 10^{18} \text{cm}^{-3}$ and 23.5 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively is measured. This behavior clearly indicates that Ga-rich conditions are advantageous for improved p-type doping.

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[*] On leave from Universitade de Sao Paulo, Sao Paulo, Brazil

## EXPERIMENTAL

Carbon doped cubic GaN epilayers were grown by rf-plasma-assisted MBE on semi-insulated GaAs (001) wafers (3 inch) at 720°C. Carbon doping was accomplished by electron beam (e-beam) evaporation of a graphite rod and adjusting the applied e-beam power. The carbon flux was calibrated by means of growing C–doped Gallium Arsenide, assuming a similar sticking coefficient of C on GaAs and GaN. Comparison of the Hall values of hole concentration and mobility of the GaAs:C samples with literature allowed an estimate of carbon concentration and compensation in our GaAs:C layers [8]. As a result of this calculation, a carbon incorporation of $2x10^{20}$ cm$^{-3}$ should possibly be achieved in GaN. This was confirmed with Secondary Ion Mass Spectroscopy (SIMS), where indeed a carbon concentration of $2x10^{20}$ cm$^{-3}$ was measured [2].

4x4 mm$^2$ square shaped samples were cleaved out at selected positions of the C-doped cubic GaN wafer for electrical characterization. Hall Effect measurements were performed at room temperature (RT) using Van der Pauw geometry and a magnetic field of 0.8 T. Photoluminescence (PL) measurements were performed in a standard system at RT. Optical measurements of the surface were carried out by an optical microscope and a scanning electron microscope (SEM). The thickness of the c-GaN:C epilayer was 750 nm.

## RESULTS AND DISCUSSION

The surface of the 3-inch wafer was checked by optical microscopy showing two different regions. In the central part with an radius of about 14 mm the density of Ga droplets was below our detection limit of about $1x10^5$ cm$^{-2}$. Outside this central part a lot of Ga droplets were observed with the density of Ga droplets increasing with increasing distance from the center. Figure 1 shows the density of Ga droplets versus the distance from the center of the wafer (full blue squares and left scale). This clearly indicates that Ga-rich growth conditions were predominating at the outer area and that the Ga excess at the surface is increasing with the distance from the wafer center [9]. For the Ga-gradient at the wafer surface two reasons are responsible. The first effect may be due to a variation of the Ga flux, which is however radially symmetric and is maximized at the center of the wafer. The second effect is the variation of the surface temperature over the wafer with the hottest spot at the center (temperature difference about 3°C in the central region of a diameter of 60 mm). The higher temperature at the center of the wafer results in an enhanced Ga desorption at the center area. At the edge of the wafer the lower temperature prevents Ga desorption and the Ga excess forms the Ga droplets during the cool down process. For that reason at different radial positions on the wafer c-GaN growth was performed under varying growth conditions from N-rich to stoichiometric and finally to Ga-rich growth conditions. In this way the incorporation of C in cubic GaN under varying Ga-excess can simply be studied by measuring the spatial variation of the electrical properties. The exact stoichiometric growth conditions were adjusted by reflection high energy electron diffraction (RHEED) at a distance of about 15 mm from the wafer center.

On small 4 x 4 mm$^2$ pieces selected from the two different regions of the wafer Hall effect measurements were carried out at RT. Samples taken from the inner part of the wafer were n-type with a carrier concentration of about 1-2 x $10^{18}$cm$^{-3}$ whereas all samples taken from the outer Ga-rich area, showed p-type conductivity. The hole concentration measured for the different samples (full circles) is plotted versus the relative position of the pieces on the wafer in Fig. 1. This behavior clearly indicates that Ga-rich conditions were advantageous for improved p-type
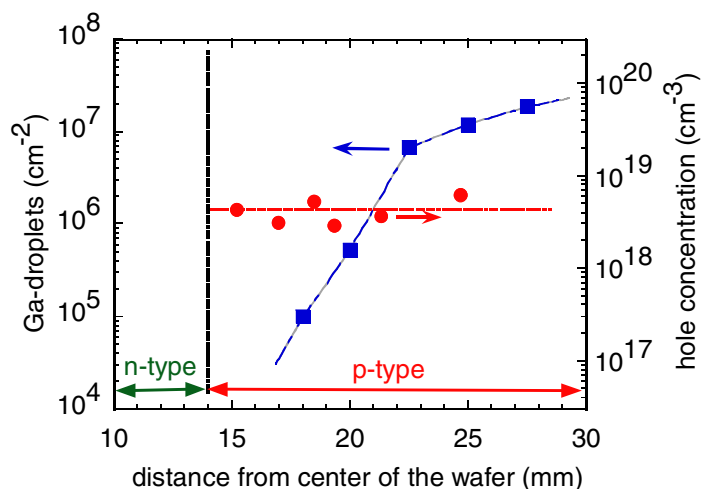
**Figure 1.** *Density of Ga droplets (squares) and hole concentration (circles) at room temperature versus the distance from the center of the wafer of a C-doped cubic GaN epilayer (C-flux: $1x10^{12}cm^{-2}s^{-1}$). (Left vertical axis: Ga-droplets density, right vertical axis: hole concentration) The full and dotted curves are guides for the eye. At a distance of about 14 mm the conductivity changes from n-type to p-type.*

doping. The hole concentration measured is the highest hole concentration ever reported for C-doped GaN epilayers and is one order of magnitude higher than the value reported on samples grown under stoichiometric conditions [2]. In addition the hole concentration is nearly independent of the Ga flux at very high Ga fluxes (dotted line in Fig.1), indicating that the C-flux is the limiting quantity for the hole concentration as discussed later.

In Figure 2 the hole concentration measured by Hall effect is plotted versus carbon flux for both the stoichiometric growth conditions and for our wafer grown under Ga-excess. At a C-flux of about $2x10^{11}cm^{-2}s^{-1}$ an increase of the hole concentration by more than 3 orders of magnitude
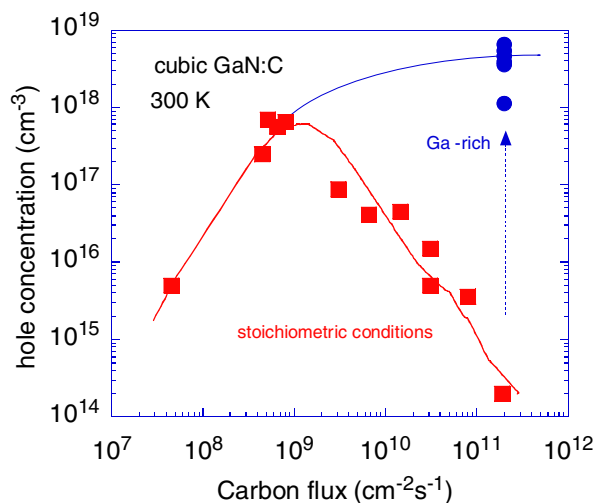


**Figure 2.** *Hole concentration at room temperature versus carbon flux for stoichiometric growth conditions (full red squares) and for growth under extrem Ga excess (full blue dots).*

is measured. To determine the degree of compensation in our C-doped cubic GaN the hole mobility is plotted versus hole concentration in Fig. 3. Full circles represent the samples grown under Ga-rich growth conditions whereas full squares represent samples grown under stoichiometric conditions. The full curves are calculated RT mobility values as a function of hole concentration for varying compensations $\Theta = N_D^+/N_A^-$. In this calculation contributions of polar optical phonon scattering, acoustic phonon scattering and ionized impurity scattering have been taken into account. The best agreement between the experimental data and the theoretical calculations indicate that the compensation ratio is about 0.6 and is almost the same for both kinds of samples. However, for the samples with the highest hole concentration a small increase of the compensation ratio is observed indicating the begin of the incorporation of additional compensating defects. The start off of the incorporation of the additional compensating deep centers under Ga-rich growth conditions occurs however at a C-flux which is about two orders of magnitude higher than that under stoichiometrical growth conditions. Probably the excess of Ga during growth forces the C to be incorporated at N sites in agreement with the suggestion made by Seager et al. [7]. Therefore, Ga-rich growth conditions enables the achievement of the high hole concentration.

Considering the amount of carbon incorporated in the GaN the ratio between the Ga-flux and the C-flux during growth was about 0.014. Therefore, the maximum number of carbon atoms incorporated in the structure is in the order of $6 \times 10^{20}$ cm$^{-3}$. As mentioned before, in a stoichiometrically grown c-GaN sample doped with a similar C-flux SIMS measurements showed indeed a Carbon concentration of about $2 \times 10^{20}$ cm$^{-3}$ [2]. Taking into account that at RT only a few percent of the incorporated C is thermally activated and that the compensation ratio is about 0.6 a value of $6 \times 10^{18}$ cm$^{-3}$ is estimated for the free hole concentration. This value is in excellent agreement with the experimental data ($p_{max} = 6 \times 10^{18}$ cm$^{-3}$) and signifies that the quantity of hole concentration is limited by the flux of our carbon source.
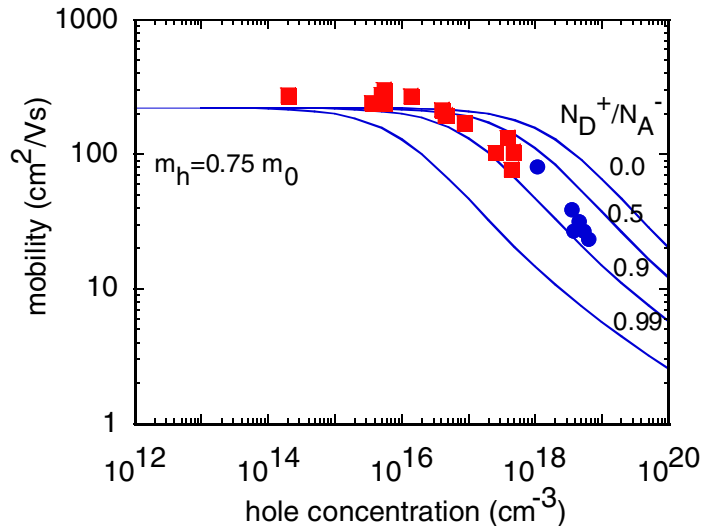


**Figure 3.** *Mobility versus hole concentration of C-doped c-GaN epilayers. Full blue circles and full red squares represent samples grown under Ga-rich and stoichiometric conditions, respectively. Full curves are calculated RT mobility values as a function of hole concentration for varying compensations $\Theta = N_D^+/N_A^-$.*

Figure 4 depicts a room temperature photoluminescence (PL) spectrum of the C-doped cubic GaN grown under Ga-rich conditions. The spectrum consists of two clearly separated emission bands at 3.2 eV and a red band at about 2.1 eV. The appearance of the red band is typical of highly C-doped c-GaN samples and is attributed to a superposition of the recombination between a deep C-related defect level, located at 1.185 eV below the conduction band, and the shallow C-acceptor and the valence band [5, 10]. Wright proposed a $C_I$-$C_N$ complex [6] for the deep donor like defect, which acts as compensating recombination center and by-passes the near band edge recombination. The 3.2 eV peak is attributed to the near band edge emission [11]. One may expects that the shallow C-related acceptor transition shall affect the edge emission, however at 300 K the acceptor luminescence is thermalized and only the band edge emission is seen [2].

As indicated in the inset of Fig.4 the intensity ratio of the red luminescence to the band edge related luminescence decreases only slightly with increasing Ga droplet density. This supports the idea that at higher Ga droplet densities, more C is incorporated at N-sites, although the compensation due to the deep complex is still severe.

In carbon doped c-GaN grown under stoichiometric growth conditions the integral luminescence intensity measured was totally quenched at very high C-concentration [12]. For Ga-rich growth conditions, however, the quenching of the luminescence was neutralized and a clear spectrum was observed as seen in Fig. 4. The restoration of the PL intensity at RT indicates that excess Ga flux does improve C incorporation, but it improves it with respect to all forms. In fact, the compensation ratio increases for the high C samples indicating that carbon is incorporated also on other sites such as carbon interstitials, C on Ga site or $C_I$-$C_N$ complexes. The improvements of the crystal quality leads to a reduction of the incorporation of non-radiative defects. The suppression of the non-radiative defects may also be responsible for the increase of the measured hole concentration. In stoichiometrically grown c-GaN a detailed optical and x-ray diffraction studies on the C incorporation showed a clear correlation between crystalline quality of the epilayer and C incorporated on N-site [3]. Detailed investigations also on Ga-rich samples are under way.
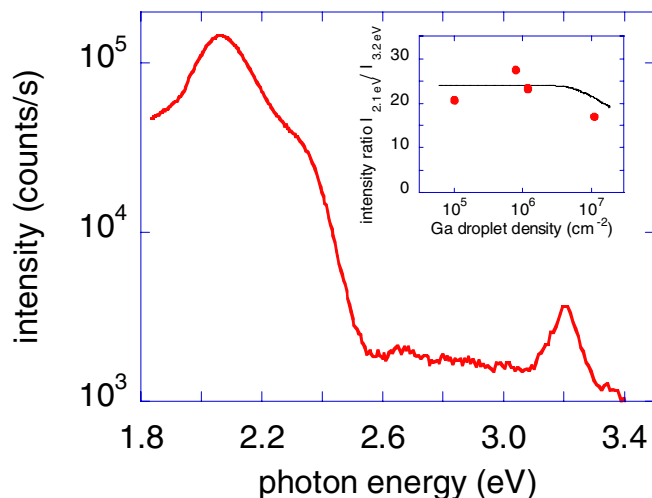


**Figure 4.** *Room temperature PL spectrum of a GaN:C samples grown under Ga-rich conditions. The inset shows the intensity ratio of the red band (2.1 eV) to near band edge luminescence (3.2 eV) as a function of the Ga droplet density.*

## CONCLUSION

Successful p-type doping by carbon of cubic GaN epilayers grown by MBE under extrem Ga excess is reported. A record hole concentration and hole mobility as high as $6.1 \times 10^{18}$ cm$^{-3}$ and 23.5 cm$^2$V$^{-1}$s$^{-1}$, respectively is measured by Hall effect at room temperature. This high hole concentration indicates that more carbon atoms are indeed incorporated on N sites and act as shallow acceptor. The measured RT hole concentration is further in excellent agreement with the value estimated by thermal activation of the C acceptor. By plotting the room temperature mobility values as a function of hole concentration a compensation ratio of about 0.6 is determined. PL-measurements showed a clear enhancement of the integral luminescence of cubic GaN:C grown under Ga excess in comparison to that grown under stoichiometrical conditions. Both the near band edge luminescence and the red band are clearly measurable at room tempreature. This behavior unambiguously indicates the improved crystal quality due to the increased incorporation of C on substituional N-sites. Our results verifies that Ga-rich conditions are advantageous for the incorporation of C on N-sites, which enables effective p-type doping of c-GaN.

## ACKNOWLEDGEMENTS

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