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A. Zado<sup>a,\*</sup>, E. Tschumak<sup>a</sup>, J.W. Gerlach<sup>b</sup>, K. Lischka<sup>a</sup>, D.J. As<sup>a</sup>

<sup>a</sup> University of Paderborn, Department of Physics, Warburger Straße 100, D-33098 Paderborn, Germany
<sup>b</sup> Leibniz-Institut f
ür Oberfl
ächenmodifizierung e.V., Permoserstraße 15, D-04318 Leipzig, Germany

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ABSTRACT

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We report on carbon doping of cubic GaN by  $CBr_4$  using plasma-assisted molecular beam epitaxy. Cubic GaN:C samples were doped at different  $CBr_4$  beam equivalent pressures between  $2 \times 10^{-9}$  and  $6 \times 10^{-6}$  mbar. The incorporated carbon concentration of up to  $1 \times 10^{20}$  cm<sup>-3</sup> was achieved in c-GaN:C as measured by secondary ion mass spectroscopy. The net donor/acceptor concentration was obtained by evaluation of capacitance-voltage data. Capacitance-voltage measurements on nominally undoped cubic GaN showed n-type conductivity. With an increase in CBr<sub>4</sub> flux the conductivity type changed to p-type and for highest CBr<sub>4</sub> flux an acceptor surplus of  $1 \times 10^{19}$  cm<sup>-3</sup> was obtained. The electrical properties of the c-GaN:C layers were investigated by current–voltage measurements and a decrease in the serial conductance by two orders of magnitude was demonstrated in c-GaN:C. A blue shift of the 2 K donor–acceptor pair luminescence with an increase in carbon concentration was obtained.

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CRYSTAL GROWTH

## 1. Introduction

For advanced optoelectronic and electronic devices controlled p-type doping and high hole mobility are necessary. Recently carbon has received considerable interest as an alternative acceptor in GaN for Mg due to its similarity to nitrogen in atomic radius and electronegativity. However, as an amphoteric dopant, carbon incorporated in GaN can act as a donor or as an acceptor. Although for doping of GaN with carbon especially tetrabromide (CBr<sub>4</sub>) as a dopant source shows great potential [1–2], no p-type conductivity of hexagonal GaN:C with CBr<sub>4</sub> has been published till date.

In this paper we report the growth of heavily carbon doped cubic GaN(c-GaN:C) using CBr<sub>4</sub>. The effect of carbon dopants on electrical capacitance–voltage (CV) and current–voltage (IV) and optical photoluminescence (PL) properties was investigated.

## 2. Experimental

Carbon doped cubic GaN layers were deposited on freestanding 3C–SiC by plasma assisted molecular beam epitaxy (MBE) under Ga rich conditions. The doping concentration of 3C–SiC was  $n=1.8 \times 10^{18}$  cm<sup>-3</sup> measured by the Hall effect. The carbon source was a CBr<sub>4</sub> sublimation source connected directly to the MBE chamber. No carrier gas was used and the CBr<sub>4</sub> flux was set by a high precision needle valve at constant source temperature of 20 °C. First a 70-nm-thick undoped c-GaN buffer layer was deposited to adjust the growth conditions followed by a 550-nm-thick GaN:C

layer. Five c-GaN:C samples grown at CBr<sub>4</sub> beam equivalent pressure (BEP) between  $2 \times 10^{-9}$  and  $6 \times 10^{-6}$  mbar and an undoped c-GaN layer as a reference were investigated.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to quantify the carbon incorporation behavior. The carbon concentration was calibrated via a reference sample in which a defined amount of carbon was built in by ion implantation. The carbon content increases sublinearly with CBr<sub>4</sub> BEP. The reason for this is under investigation. Due to the high conductivity of the 3C-SiC substrates the doping concentration of our samples cannot be obtained by the Hall effect measurements. Thus, the net donor  $N_D - N_A$  and acceptor  $N_A - N_D$  concentrations were calculated using capacitance-voltage (CV) data [3]. CV measurements were performed on metal-insulator-semiconductor (MIS) structures at 1 MHz and 50 mV AC level by an Agilent Precision LCR Meter E4980A. The insulation layer of the MIS structures was 100-nmthick Si<sub>3</sub>N<sub>4</sub>, which was produced by plasma enhanced chemical vapor deposition (PECVD). For the metal contact of the MIS structures 15 nm Ni and 50 nm Au were thermally evaporated on top of the insulator. Large area ohmic contacts at the back side of the samples were prepared by soldering with In.

For conductivity investigations of c-GaN:C an Agilent Precision Semiconductor Parameter Analyzer 4156C was used. IV measurements through the sample vertical to the surface were performed. Ti/Ni/Au (15/15/50 nm) was thermally evaporated to form ohmic contacts on top of c-GaN:C. The contacts had a diameter of 300  $\mu$ m. The reverse sample side was connected with large area solder In contact.

PL measurements were performed in a He bath cryostat at 2 K. The luminescence was excited by a HeCd UV laser with a power of 3 mW and was measured in a standard PL system.

<sup>\*</sup> Corresponding author. Tel.: +49 5251605829; fax: +49 5251605843. *E-mail address*: a.zado@uni-paderborn.de (A. Zado).

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#### 3. Results and discussion

Fig. 1 shows the incorporated carbon concentration vs.  $CBr_4$  beam equivalent pressure. The carbon incorporation in c-GaN increases with an increase in  $CBr_4$  BEP. A maximum carbon incorporation of  $1 \times 10^{20}$  cm<sup>-3</sup> was reached with our system without diminishing effect on the structural properties of the c-GaN crystal.

The net donor  $N_D - N_A$  and acceptor  $N_A - N_D$  concentration of the samples was calculated from CV data using Eq. (1.1),

$$N_{CV} = \frac{2}{q\varepsilon_s} \left( -\frac{d(1/C^2)}{dV} \right)^{-1}$$
(1.1)

where  $\varepsilon_s$  is the dielectric constant of the semiconductor. The calculated  $N_{CV}$  data are plotted vs. CBr<sub>4</sub> beam equivalent pressure in Fig. 1. The net dopant concentration values with donor surplus are indicated by squares and with acceptor surplus by circles. The net donor concentration of the undoped c-GaN was approximately  $10^{17}$  cm<sup>-3</sup>. At low concentrations the incorporated carbon causes a decrease in the net donor concentration  $N_D - N_A$ . At CBr<sub>4</sub> BEP around  $2 \times 10^{-8}$  mbar the incorporated carbon produces an acceptor surplus in c-GaN:C and at higher carbon density the net acceptor concentration increases with an increase in CBr<sub>4</sub> BEP. SIMS measurements revealed that the density of incorporated carbon s at least one order of magnitude higher than the net donor/ acceptor density  $N_{CV}$ . We assume that about 10% of the incorporated carbon act as acceptors whereas about 90% form self-compensated defects as discussed in [3] in detail.

Fig. 2 shows the serial conductance  $G_s = 1/R_s$  of the carbon doped samples vs. CBr<sub>4</sub> beam equivalent pressure. For this investigation, IV curves were measured between -5 and 5 V. All curves showed a slightly non-ohmic behavior. The serial conductance was determined from the linear part of the IV curves at positive voltages. The conductance of samples with donor surplus is indicated by squares and of samples with acceptor surplus by circles. The dashed lines are guides for the eye. Up to a CBr<sub>4</sub> BEP of about  $1 \times 10^{-7}$  mbar carbon doping of c-GaN causes a decrease in the sample conductivity. c-GaN:C samples grown with higher CBr<sub>4</sub> BEP offer



**Fig. 1.** Incorporated carbon concentration (diamonds) and net carrier concentration  $N_{CV}$  (squares and dots) vs. CBr<sub>4</sub> beam equivalent pressure. The dashed lines are guides for the eye.



**Fig. 2.** Serial conductance vs. CBr<sub>4</sub> beam equivalent pressure. Serial conductance of samples with donor and acceptor surplus is indicated by squares and dots, respectively. The dashed lines are guides for the eye.

increase in serial conductance. It is noticeable that the serial conductance of samples with acceptor surplus of  $1.0 \times 10^{18}$  and  $4.5 \times 10^{18}$  cm<sup>-3</sup> is one order of magnitude lower than that of the c-GaN:C with the lowest donor surplus of  $4.4 \times 10^{16}$  cm<sup>-3</sup>. Additionally, the serial conductance of the c-GaN:C sample with highest net acceptor concentration of  $N_A - N_D = 1 \times 10^{19}$  cm<sup>-3</sup> is one order of magnitude lower than the conductance of the undoped sample with net donor concentration of  $N_D - N_A = 2.7 \times 10^{17}$  cm<sup>-3</sup>. We explain this result by extremely low hole mobility caused by ionized impurity scattering and compensation effects [4] and assume that the conductivity of the c-GaN:C sample with lowest net acceptor concentration of  $1.0 \times 10^{18}$  cm<sup>-3</sup> is affected by electron conduction.

Fig. 3(a) shows PL spectra of differently doped c-GaN:C layers measured at 2 K. For better clarity, the intensity of the excitonic transition at 3.27 eV is normalized to 1 and the spectra are offset to each other. In all samples only the lines of undoped c-GaN at 3.27 eV (exciton (X) transition) and around 3.15 eV (donor-acceptor pair  $(D^0A^0)$  transition) were measured. No carbon related PL lines at 3.08 eV [5,6] were observed in c-GaN:C samples. However, a deep luminescence centered around 2 eV was measured in all carbon doped layers (not shown here). A feature of the c-GaN:C samples is the blue shift of the  $(D^0A^0)$  transition energy with increased CBr<sub>4</sub> BEP. This behavior can be explained by the amphoteric nature of carbon dopants. Assuming that a part of carbon atoms replaces Ga and acts as donator with similar activation energy as residual oxygen of 28 meV [7] the increase in the peak position to higher energies can be explained by increased donor concentration as it was found for Si dopants [8]. This is verified by increase in the  $(D^0A^0)$  peak intensity of c-GaN:C with an increase in  $CBr_4$  BEP as shown in Fig. 3(b).

## 4. Conclusions

Carbon doping of cubic GaN:C was realized using CBr<sub>4</sub> as a carbon source. An incorporated carbon concentration of  $1 \times 10^{19}$  cm<sup>-3</sup> was achieved without degradation of the crystalline properties of c-GaN.



**Fig. 3.** (a) Low-temperature photoluminescence spectra of investigated carbon doped c-GaN:C layers. The intensity of the X-transition at 3.27 eV is normalized to 1. The spectra are offset against each other for better clarity. (b) Relative PL intensity  $I(D^0A^0)/I(X)$  vs. CBr<sub>4</sub> beam equivalent pressure. The lines are guides for the eye.

A decrease in the net donor concentration with increased carbon concentration and a surplus of net acceptor concentration at carbon densities higher than  $10^{19}$  cm<sup>-3</sup> were observed. It was shown that carbon doping causes a decrease in c-GaN:C conductance by two orders of magnitude at carbon densities lower than  $5 \times 10^{19}$  cm<sup>-3</sup>. At higher carbon densities the conductance of c-GaN:C increases again. Photoluminescence measurements showed a shift of the donor-acceptor peak position to higher energies indicating the amphoteric behavior of carbon dopants.

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