

Carbon doping of cubic GaN under gallium-rich growth conditions

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Successful p-type doping of cubic GaN by carbon grown under Ga-rich conditions is reported with maximum hole concentration of $6 \times 10^{18} \text{ cm}^{-3}$ and hole mobility of $19 \text{ cm}^2/\text{Vs}$ at room temperature, respectively. Cubic GaN:C was grown by rf-plasma assisted molecular beam epitaxy (MBE) on a semiinsulating GaAs (001) substrate (3 inches wafer). C-doping of the c-GaN was achieved by e-beam evaporation of a graphite rode with an C-flux of $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Optical microscopy, Hall-effect measurements and room temperature photoluminescence were used for the investigation of the morphological, electrical and optical properties of cubic GaN:C. Under Ga-rich growth conditions most part of the carbon atoms were incorporated substitutionally on N-site giving p-type conductivity. Our results verify that effective p-type doping of c-GaN can be achieved under Ga-rich growth conditions.

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1 Introduction For the development of electronic and optoelectronic devices, based on the group III–V nitrides, techniques to control the doping process are crucial. The most common impurity to achieve p-type doping in cubic gallium nitride (c-GaN) is magnesium (Mg), with a maximum concentration of holes of about $6 \times 10^{17} \text{ cm}^{-3}$. The high acceptor ionization energy and compensation effects however avoid a considerable increase of this value [1]. Therefore, alternative dopant impurities are intensively looked for and carbon (C) is heavily discussed as an very attractive alternative acceptor due to its similarity to nitrogen (N) in both atomic radius and electronegativity [2].

Previous experiments by Abernathy et al. [3] 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 reported.

In a previous work we succesfully doped c-GaN by carbon and reached a hole concentration and a hole mobilities of $6 \times 10^{17} \text{ cm}^{-3}$ and $200 \text{ cm}^2/\text{Vs}$ at room temperature, respectively [2]. These samples were grown under stoichiometric conditions by molecular beam epitaxy (MBE). Unfortunately due to self-compensation effects the hole concentration saturated and then decreased with increasing C-flux. Wright [5] proposed that a $\text{C}_\Gamma\text{-C}_\text{N}$ complex is most likely responsible for the observed compensation in our samples. However under Ga-rich growth conditions C shall preferably be incorporated at the N substitutional site, acting as an acceptor. This idea was supported by the results of Seager et al. [6], who

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found in intentionally Si-doped hexagonal GaN samples, containing various concentrations of carbon, that most of the carbon sat in N site. Therefore, in this contribution we extend our previous study and investigate the incorporation of C under Ga-rich growth conditions.

2 Experimental Carbon doped cubic GaN epilayers were grown by rf-plasma-assisted MBE on semi-insulated GaAs (001) wafers (3 inches). Carbon doping was achieved by electron beam (e-beam) evaporation of a graphite rod, with the e-beam power maintained at 230 W during growth. The C-flux was calibrated externally by growing C-doped GaAs epilayers and measuring the hole concentration and hole mobilities at room temperature (RT). These values and the compensation factor in GaAs [7], let us determine the C-flux assuming the same sticking coefficient for both GaAs and c-GaN. For the used e-beam power of 230 W a C-flux of $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ was estimated. At selected positions of the C-doped cubic GaN wafer $4 \times 4 \text{ mm}^2$ squares were cleaved out for electrical characterization in Van der Pauw geometry with a magnetic field of 0.8 T at RT. 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.

3 Results and discussion

3.1 Optical investigations of the surface Optical microscopy of the surface showed two different regions. In the central area of the 3-inch wafer with an radius of about 14 mm the number of Ga droplets was below our detection limit of about $1 \times 10^5 \text{ cm}^{-2}$. The rest of the wafer was covered with a lot of Ga droplets and the density of Ga droplets increased by more than two orders of magnitude with increasing distance from the center. In Fig. 1 the number of Ga droplets is plotted versus the distance from the center of the wafer (full squares and left scale). The solid curve is a guide for the eye. It indicates that the Ga excess at the surface is increasing at the outer edge of the wafer and that in this area Ga-rich growth conditions were predominating [8]. Two reasons are responsible for this Ga gradient at the wafer surface. First the Ga flux itself has a radial distribution across the wafer and second a temperature gradient exists with the hottest spot at the center. 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. Therefore by measuring the spatial variation of the electrical properties the incorporation of C in cubic GaN can be studied under varying Ga-excess conditions. 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.

3.2 Electrical measurements Hall effect measurements were carried out at RT on small $4 \times 4 \text{ mm}^2$ pieces selected from the two different regions of the wafer. As can be seen in Fig. 1 (full circles) pieces from the outer area with excess of gallium showed p-type behavior whereas samples from the inner part

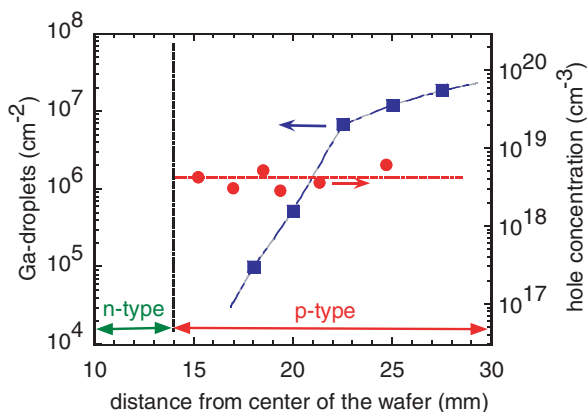


Fig. 1 (online colour at: www.interscience.wiley.com) Density of Ga droplets (squares) and hole concentration (circles) at room temperature versus the distance from the center of the wafer of a C-doped cubic GaN epilayer (C-flux: $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$). (Left vertical axis: Ga-droplet 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.

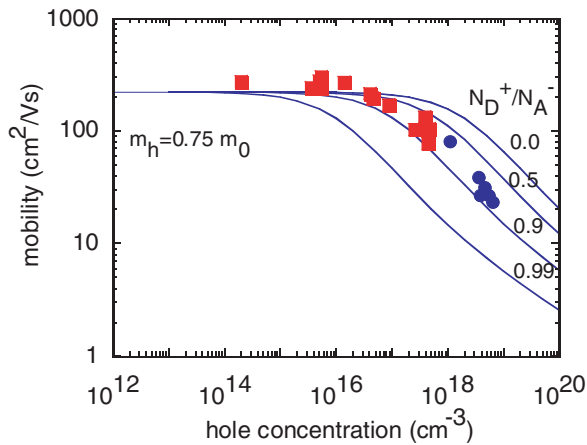


Fig. 2 (online colour at: www.interscience.wiley.com) Mobility versus hole concentration of C-doped c-GaN epilayers. Full circles and full squares represent samples grown under Ga-rich and stoichiometric conditions, respectively. Full curves represent calculated RT mobility values as a function of hole concentration for varying compensations $\theta = N_D^+/N_A^-$.

of the wafer were n-type. This behavior clearly indicates that Ga-rich conditions were advantageous for improved p-type doping. The maximum hole concentration measured was $6 \times 10^{18} \text{ cm}^{-3}$ with a hole mobility of $19 \text{ cm}^2/\text{Vs}$, respectively. This is the highest hole concentration reported for C-doped GaN epilayers and is one order of magnitude higher than the value reported from similar epilayers grown under stoichiometric conditions [2].

In Fig. 1 the hole concentration measured for the different samples (full circles) is plotted versus the relative position of these pieces on the wafer. One clearly sees that the hole concentration is nearly independent of the Ga-droplet density and shows only a slight increase with increasing Ga-excess (dotted line in Fig. 1). 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 $6 \times 10^{20} \text{ cm}^{-3}$. Taking into account that at RT only 1% of this amount is thermally activated a value of $6 \times 10^{18} \text{ cm}^{-3}$ is estimated for the free hole concentration which is in excellent agreement with the experimental data ($p_{\text{max}} = 6 \times 10^{18} \text{ cm}^{-3}$). It signifies that the quantity of hole concentration is limited by the flux of our carbon source. These results further indicate, that for the part of the wafer grown with excess of Ga most of the carbon is incorporated at the N site resulting in p-type conductivity. The central area of the wafer was also electrically characterized. All pieces showed n-type behavior.

In Fig. 2 the RT hole mobility of all our C-doped c-GaN epilayers is plotted versus hole concentration (full symbols). Full circles represent the samples grown under Ga-rich growth conditions whereas full squares represent samples grown under stoichiometric conditions. The full curves represent 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 three 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. [6]. Therefore, Ga-rich growth conditions enables the achievement of the high hole concentration.

3.3 Photoluminescence measurements Photoluminescence (PL) measurements carried out at RT showed a clear band edge luminescence at 3.2 eV and a red band at about 2.1 eV (see Fig. 3). This kind of spectra were observed in GaN:C samples with high C-flux and is shown in Fig. 3 [9, 10]. However, whereas under stoichiometric growth conditions the near band edge luminescence was totally suppressed

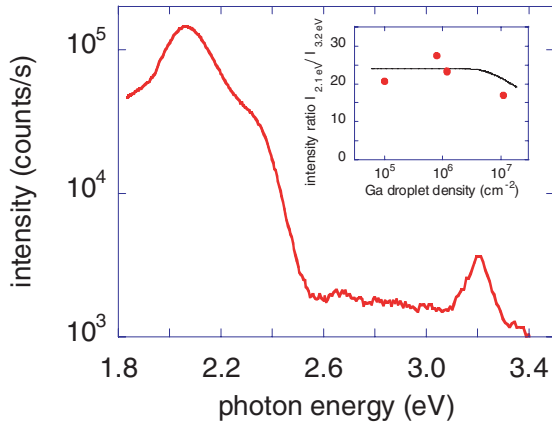


Fig. 3 (online colour at: www.interscience.wiley.com) PL spectrum at RT from a GaN:C sample grown under Ga-rich conditions. In the inset the intensity ratio of the red band (2.1 eV) to near band edge luminescence (3.2 eV) is plotted versus Ga droplet density.

this band reappeared under Ga-rich growth conditions [11]. The red luminescence was attributed to a superposition of the recombination between a deep C-related donor center, located at 1.185 eV below the conduction band, and the shallow C-acceptor and the valence band [11]. Wright proposed a $C_{\Gamma}-C_N$ complex [5], which acts as compensating recombination center and by-passes the near band edge recombination. As indicated in the inset of Fig. 3 the intensity ratio of the red luminescence to the band edge related luminescence decreases slightly with increasing Ga droplet density. This supports the idea that at higher Ga droplet densities, more C is incorporated at N-sites.

4 Conclusions We report successful p-type doping by Carbon of cubic GaN epilayers grown by MBE under Ga-rich growth conditions. A maximum hole concentration of $6 \times 10^{18} \text{ cm}^{-3}$ and hole mobility of $19 \text{ cm}^2/\text{Vs}$ is measured at room temperature. This high hole concentration indicates that most of the carbon is indeed incorporated on N sites and acts as shallow acceptor. The measured RT hole concentration is further in excellent agreement with the value estimated by thermal activation of the C acceptor. Our results verifies that effective p-type doping of c-GaN can be achieved under Ga-rich growth conditions.

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