STUDIES ON CARBON AS ALTERNATIVE P-TYPE DOPANT FOR GALLIUM NITRIDE

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Abstract

GaN layers were grown by molecular beam epitaxy and doped with carbon of nominal concentrations ranging from 10^{16} cm^{-3} to 10^{20} cm^{-3}. The incorporation of carbon leads to a reduction of the background electron concentration by one order of magnitude but the material remains n-type. For high carbon concentrations a re-increase of the carrier concentration is observed which is related to selfcompensation. Investigations of the donor-acceptor-pair luminescence show that doping with carbon is accompanied by the generation of a new donor exhibiting a thermal activation energy of about 55 meV. Layers grown by atomic layer epitaxy are marked by an increased intensity of the donor-acceptor-pair band luminescence which is attributed to the enforced incorporation of carbon onto the nitrogen sublattice. The yellow luminescence is found to be a typical feature of all carbon doped layers in contrast to nominally undoped samples.

Introduction

The realization of electronic and optoelectronic devices such as heterojunction bipolar transistors and laser diodes, requires the control of dopant profiles as well as a high p-type conductivity. P-type doping of GaN and of other wide-bandgap semiconductors is in general difficult to achieve and not yet well understood. A compensation mechanism likely induced by a high energy gain caused by an electron transfer from a donor state to an acceptor state with gain values close to the bandgap value is discussed as one of the most important reasons [1].

Today, magnesium is widely used for p-type doping of GaN due to its relatively low thermal activation energy of approx. 170 meV compared to other group II dopants such as Zn, Hg and Cd. Hole concentrations of up to 10^{18} cm^{-3} at room-temperature (RT) are attainable. However, magnesium features several disadvantages like its limited solubility in GaN, its high vapour pressure and low sticking coefficient, its tendency for segregation and diffusion and a low ionization ratio of about one percent at RT. As a result of the latter high magnesium concentrations are necessary in the layers which consequently leads to low mobilities and hence conductivity's. In hydrogen containing growth environments magnesium acceptors are passivated due to the formation of neutral Mg-H complexes. As a result, an additional post-growth treatment like thermal annealing or low energy electron beam irradiation is required to achieve p-type conductivity. Passivation by hydrogen is reported for the dopants calcium [2] and carbon [3] as well.

Alternative group II dopants have recently been investigated. P-type GaN was achieved by implantation of Ca and its ionization energy was determined to 169 meV [2]. Beryllium received some interest and p-type conductivity was obtained in cubic GaN when it is was codoped with oxygen [4, 5]. Theoretical calculations confirm the advantage of the codoping

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method and predict an ionization energy of 60 meV for the beryllium acceptor in wurtzite GaN [6].

Group IV elements can form acceptors or donors in GaN depending on whether they are located on the nitrogen or gallium sublattice, respectively [7]. As it is known from GaAs, this amphoteric behaviour critically depends on the growth conditions [8]. Especially carbon has received a considerable interest as a possible p-type dopant in GaN. It should preferentially occupy nitrogen sites due to its similarity to nitrogen in terms of atomic radius and electronegativity. Moreover, it has proved to be a highly efficient acceptor in GaAs featuring a shallow acceptor level and high solubility as well as a low diffusion coefficient in this material. P-type conductivity of carbon doped GaN was observed for cubic material [9] whereas little is known for this dopant in wurtzite GaN. Theoretical considerations predict an excellent solubility of this element in GaN [1, 10] and no segregation was found in layers grown by molecular beam epitaxy (MBE) doped with a concentration of 2×10^{20} cm^{-3} [11]. Furthermore, the lack of d-electrons in carbon are assumed to result in a shallower acceptor level compared to magnesium [12]. In this paper, a study on the behaviour of carbon in wurtzite GaN is presented with the intention to check if this element can be an alternative p-type dopant to magnesium.

Experiment

GaN films were synthesized in an EPI 930 MBE system equipped with an EPI Unibulb radio frequency (rf) nitrogen plasma source. All layers were grown with a V/III flux ratio close to unity. Layers with thickness of about 1 μm were deposited on sapphire (0001) after a nitridation step and the growth of 40 nm undoped GaN which should guarantee similar nucleation conditions for all layers under investigation. The growth rate and growth temperature were 640 nm/h and 750°C, respectively. Hydrogen passivation of acceptors is not expected to occur since annealing experiments of magnesium doped samples did not change the electrical properties of these films. Carbon doping was realized by use of a resistively heated graphite filament. The density of the incorporated carbon in GaN was calculated via the growth and C doping of GaAs layers, assuming a carbon sticking coefficient of unity for both materials and an acceptor ionization ratio of unity at RT for GaAs. This results in maximum nominal carbon concentrations of about 2×10^{20} cm^{-3} in the GaN samples under investigation, limited by the maximum heating power of approx. 550 W for the carbon filament. In the following, an unintended background carbon concentration in nominally undoped GaN layers is neglected. Free carrier concentrations as well as mobility's were measured by Hall-effect in van der Pauw geometry assuming a Hall factor of unity. Photoluminescence (PL) investigations were carried out by using a HeCd laser at a wavelength of 325 nm.

Results and discussion

Undoped GaN layers grown under optimized growth conditions exhibit background electron concentrations of about 2×10^{17} cm^{-3} at RT. The ionization energy of the corresponding donor is determined to 30 meV by Hall-effect measurements. The influence of the carbon doping level on the carrier concentration is shown in Figure 1. The error bars represent the standard deviation of samples grown under identical conditions. The carrier concentration decreases with increasing nominal carbon doping levels of up to approx. 2×10^{19} cm^{-3} resulting in a compensation of about one order of magnitude. For even heavier doped layers the carrier concentration raises again. As a result, all layers under investigation remain n-type. Figure 1 also

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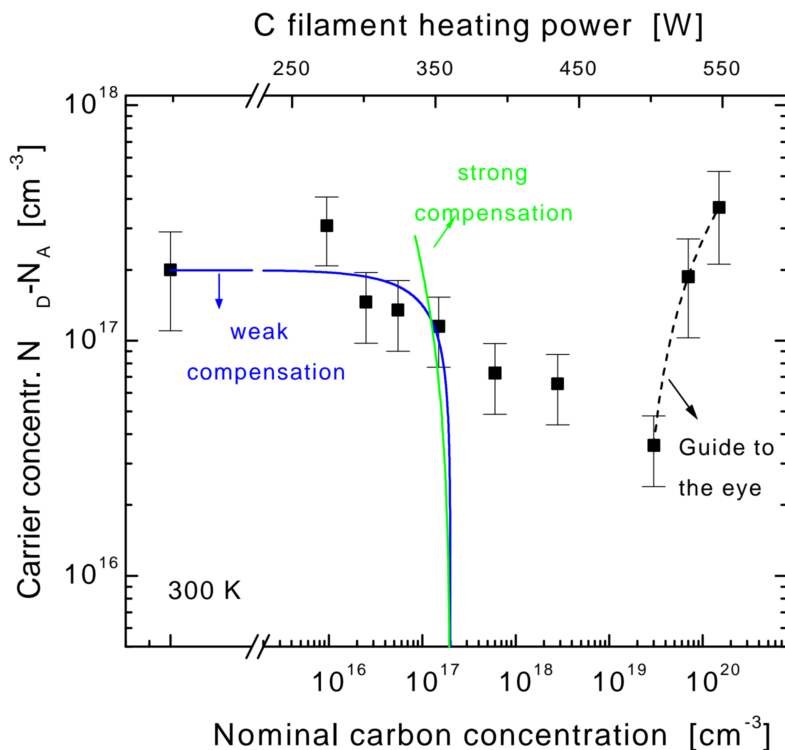

Figure 1: Room-temperature carrier concentration vs. nominal carbon concentration in GaN:C. The dashed curves correspond to the expected compensation behavior as described in the text.

contains theoretical curves for the expected dependency of the carrier concentration on the carbon doping level in compensated material, assuming that the concentration and ionization energy of the background donor remain constant with values of 2 x 10^{17} cm^{-3} and 30 meV, respectively, and that every carbon atom forms a single acceptor. The two curves correspond to the standard approximation of weak and strong compensation in a non-degenerated semiconductor and can be found elsewhere [13]. Obviously, the experimental data do not follow this simple compensation mechanism. It can be explained by assuming that only a part of the carbon atoms forms an acceptor in GaN. Referring to theoretical calculations of Boguslawski *et al.* [1, 7] and Neugebauer *et al.* [10] carbon should be preferably incorporated on a nitrogen site where it forms an acceptor. However, there is also a tendency that carbon atoms will be incorporated on Ga sites where they act as donors. Especially the formation of selfcompensating C_{Ga}-C_N pairs may occur due to the large energy gain close to the value of the band gap originating from an electron transfer from C_{Ga} to C_N. Moreover, there is a gain by the large binding energy of about 1 eV of nearest neighbor C^+-C^- pairs. As a result, this should produce a high solubility of carbon in GaN. The increase of the carrier concentration in Figure 1 can therefore be explained by the entire selfcompensation of carbon acceptors. This is also known from carbon doping of GaAs where carbon likely forms atomic clusters at high doping levels [14].

The lack of a complete carrier compensation close to the value of 2 x 10^{17} cm^{-3} and the missing of a carrier type inversion for higher carbon doping levels in Figure 1 can be explained by an accompanying generation of donors in addition to the background donors. This is supported by PL experiments indicating the formation of a deeper donor correlated to carbon. Figure 2 shows the temperature dependence of the DAP zero-phonon line intensity for two different GaN:C samples. The value of approx. 55 meV determined for the thermal activation energy is significantly higher compared to the value of the background donor. A lineshape analysis of the DAP band using this activation energy leads to an binding energy of the carbon correlated acceptor of approx. 230 meV which is about 15 meV lower than the value found for the magnesium acceptor in our GaN:Mg samples. A detailed review of the DAP analysis is given in Ref. [15].

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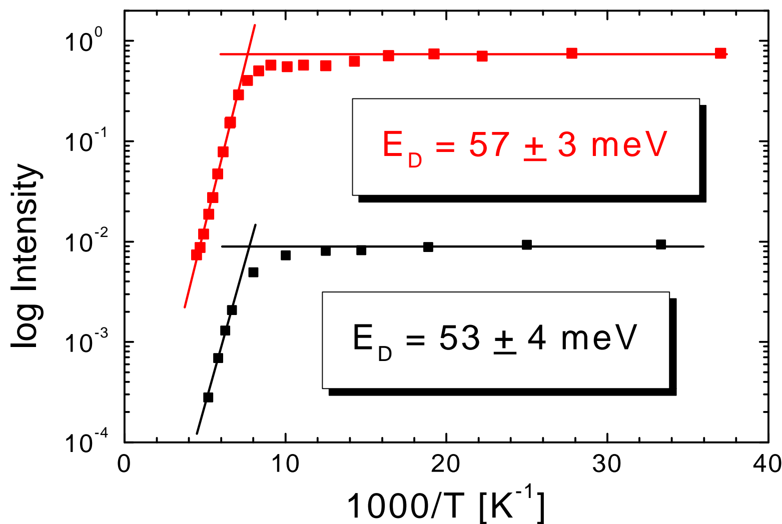

Figure 2: Arrhenius plots of the intensity of the zero phonon replica of the donor-acceptor-pair (DAP) band for two different GaN:C samples.

Room-temperature Hall mobility's of the samples from Figure 1 are shown in Figure 3. For low carbon densities a rather small effect on the mobility is expected. The decrease for carbon concentrations above 5 x 10^{16} cm^{-3} may be interpreted as scattering at ionized carbon atoms and / or at extended defects induced by the carbon doping. For doping levels above 2 x 10^{19} cm^{-3} the mobility's seem to saturate. This may be explained by a transition from isolated Coulomb scattering into dipole scattering which is theoretically predicted in Ref. [16] and experimentally verified in Ref. [17] for the method of reactive codoping where donor-acceptor complexes form the dipole similar to the predicted C^{-}-C^{+} pairs for GaN:C .In summary, the results suggest that carbon forms both a donor and an acceptor which is in good agreement with Ref. [1, 7].

To achieve p-type conductivity in GaN:C despite of the amphoteric behavior of carbon, the growth of GaN:C by atomic layer epitaxy was investigated. By subsequently supplying Ga, C and N to the growth surface by closing and opening the corresponding shutters in this sequence, the probability of carbon to incorporate on the nitrogen sublattice is hopefully increased. At the same time the formation of C^{+}-C^{-} pairs may be reduced. The PL spectrum of a sample grown by ALE is shown in Figure 4. A clear DAP band starting at 3.261 eV can be identified as well as an impurity bound exciton at 3.466 eV which is approx. 5 meV lower compared to the donor bound excition of nominal undoped samples. It is yet not clarified whether the peak at 3.455 eV is still the donor bound exciton or a superposition of both, acceptor- and donor bound exciton.

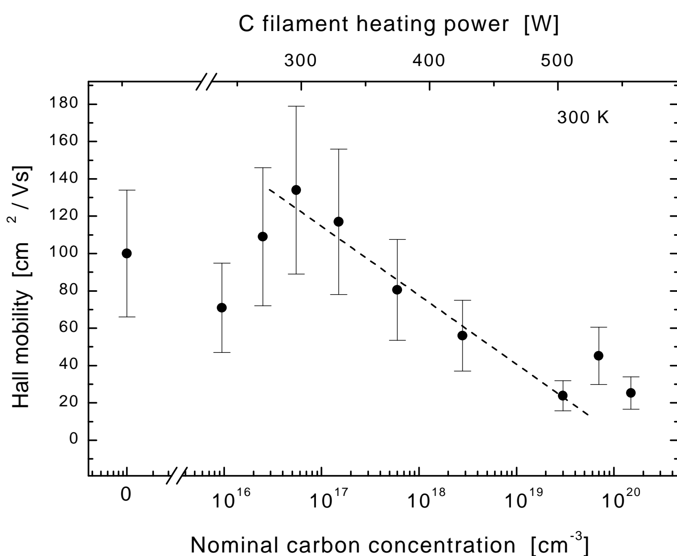

Figure 3: Room-temperature Hall mobility's vs. nominal carbon concentration of the samples from Figure 1. The line is a guide to the eye.

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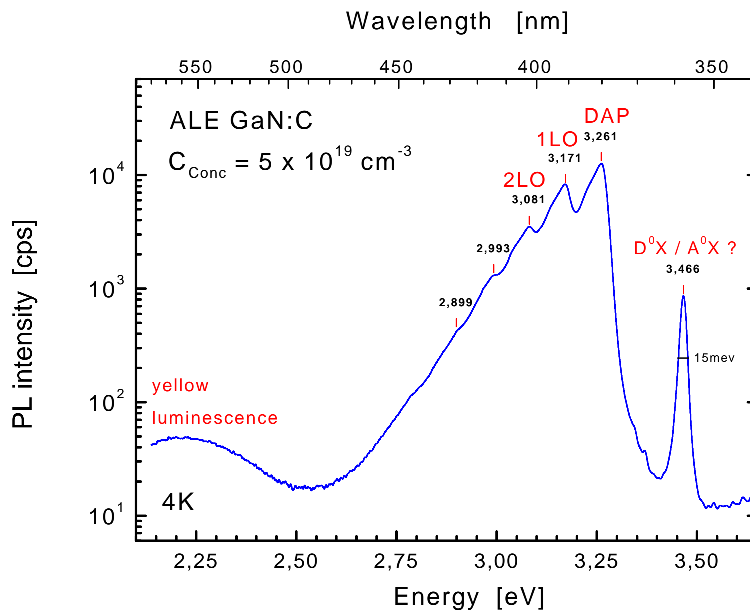

Figure 4: PL spectrum taken at 4 K of a GaN:C sample grown by ALE as described in the text. The nominal carbon concentration was 3 x 10^{19} cm^{-3}. The DAP zero-phonon-line is centered at 3.261 eV followed by its LO-phonon replicas.

The DAP recombination of this sample is more pronounced in terms of intensity and clear occurrence of the phonon replicas compared to those of conventionally carbon doped GaN layers discussed before. Electrical measurements characterize the layer to be highly resistive and the type of conduction could not be determined. This suggests that carbon can be more effectively incorporated on nitrogen sites to form an acceptor if the material is grown by ALE.

The appearance of the yellow luminescence at around 2.2 eV can be seen in Figure 4 as well. The yellow luminescence is a common feature of all grown carbon doped samples. For very high carbon doping levels the PL is sometimes even dominated by this emission. In comparison, nominally undoped as well as silicon and magnesium doped films grown in our system show a neglectabe weak yellow luminescence. Ogino and Aoki found a strong indication that the yellow luminescence is correlated to the carbon and that its intensity increases with the carbon doping level [18]. They assumed that the emission is generated by the transition between a shallow donor and a deep acceptor. They further assigned this deep level to a complex, namely C_N-V_{Ga}. In contrast, Glaser *et al.* suggested a transition between a deep donor and a shallow acceptor which they assumed to be carbon on the nitrogen site [19].

Conclusions

In summary, it was found that only a part of carbon forms an acceptor in n-type GaN resulting in a partial compensation of the background electron concentration. For doping levels above 3 x 10^{19} cm^{-3} a re-increase of the electron concentration is observed which can be explained by the formation of selfcompensating C_{Ga}-C_N pairs which is in good agreement with theoretical predictions. PL investigations of carbon doped GaN show both, the generation of a deeper donor than in undoped samples and the appearance of the yellow emission.

Up to now, carbon has not stated to be a superior dopant compared to Mg. One possible approach to achieve p-type conductivity by carbon doping is the use of alternative growth techniques like ALE to enforce carbon on the nitrogen site and to prevent selfcompensating nearest neighbor pairs. This has to be further investigated.

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