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Abstract
Carbon doping of cubic GaN epilayers has been performed by rf-plasma-assisted molecular beam epitaxy using an e-beam evaporation source. Hall-effect measurements at room temperature and low-temperature photoluminescence were used to characterize the electrical and optical properties. Room-temperature Hall-effect measurements revealed a maximum hole concentration of the c-GaN epilayer of 6×10^{17} cm^{-3} with a mobility of 200 cm^2 V^{-1} s^{-1}. With increasing e-beam evaporation power a new photoluminescence line at 3.08 eV appeared at 2 K. This line is attributed to a donor acceptor transition, 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. At high C concentrations a deep band appeared at 2.1 eV indicating compensation effects.

1. Introduction

Controlled p-type doping is crucial for the development of electronic and optoelectronic devices based on the group III–V nitrides. Up until now Mg has been the commonly used p-type dopant in the molecular beam epitaxial (MBE) growth of both hexagonal and cubic phase GaN and is the only acceptor in GaN that reproducibly generates useful p conduction. Despite this breakthrough the hole concentration in GaN:Mg has remained low, being two orders of magnitude below that of, for example, GaAs:C at a doping level of 2×10^{18} cm^{-3}. One reason for the low hole concentration is the large Mg acceptor ionization energy. Recent theoretical and experimental studies further indicate that at high dopant concentrations compensation by natural defects plays a significant role in the p-type doping process [1]. MBE growth has shown that Mg is very volatile, and requires low substrate temperatures [2] and N-rich growth conditions [3]. Both conditions are disadvantageous for the growth of high-quality epilayers, especially for the cubic phase, where N-rich conditions deteriorate the phase purity [4].

Due to the successful p-type doping of GaAs with C, carbon seems to be an appropriate candidate as an alternative acceptor for GaN. Carbon is an acceptor in GaN when substituting nitrogen [5, 6]. It is the only group IV element that has a small enough atomic radius to fit the nitrogen site. Compared with other group II acceptors such as Mg, carbon is much less volatile

and therefore not prone to causing a residual memory effect in the growth system. Theoretical calculations have found that C_N is an effective mass acceptor and that the incorporation of C on the N site is preferred. However, due to the amphoteric nature of C the concentration of C_N and C_{Ga} may be comparable. In addition, at high C concentrations the C_{Ga} and C_N have a strong tendency to form C_{Ga}^+–C_N^- nearest-neighbour pairs, leading to self-compensation [7, 8].

A previous study of carbon doping of cubic GaN grown by metal organic molecular beam epitaxy (MOMBE) on GaAs substrates indicated that carbon created shallow acceptors and p-type conductivity [9]. However, due to the use of CCl$_4$ a pronounced reduction in growth rate prohibited the incorporation of higher C concentrations.

In hexagonal GaN no successful p-type doping by C has been reported up until now. However, two different observations have been made in MBE and metal–organic chemical vapour deposition (MOCVD) grown samples. On the one side, high-quality semi-insulating C-doped GaN layers with resistivities greater than 10^6 Ωcm have been grown with high reproducibility and reliability using methane gas (cracked by an ion gun) as a carbon source by ammonia MBE [10]. Carbon doping by using a resistivity heated graphite filament in rf-plasma-assisted MBE led to a reduction of the background electron concentration by one order of magnitude but the material remained n-type [11]. On the other side, for high carbon concentration a re-increase of the electron concentration is observed, which was attributed to the introduction of a new carbon-related donor. Since carbon is present as a contaminant in most growth reactors (graphite parts) and in MOCVD processes, its unintentional role in the compensation and doping of GaN layers might nevertheless be significant. Huge amounts of carbon ($>2 \times 10^{19}$ cm^{-3}) have been found in low-pressure MOCVD using dimethylhydrazine (DMHy) as a group V source [12]. In plasma-assisted MOCVD using CH$_x$ as a carbon source, secondary ion mass spectrometry (SIMS) analysis has indicated large amounts of C and H ($\sim 10^{19}$–10^{20} cm^{-3}) in the samples [13]. After annealing under a nitrogen atmosphere, the films remained highly resistive. It was suggested that the C–H complex is thermally stable and that H may passivate the C acceptors [13]. In hydride vapour phase epitaxy (HVPE) samples it was found that the incorporation of carbon by a propane/H$_2$ mixture produces a significant yellow luminescence around 2.2 eV [14], which is similar to the yellow luminescence observed by Ogino and Aoki [15] in intentionally C doped microcrystal powder and needle-like crystals. Photoluminescence (PL) investigations on undoped n-type GaN layers grown on 6H–SiC and sapphire [16] and on Si [17] reveal the presence of residual acceptors with an optical binding energy of 230 meV, which is attributed to carbon on nitrogen sites.

In this contribution we study in detail the incorporation of C in cubic phase GaN and demonstrate the practicability of C as an alternative acceptor for p-type doping. Hall-effect measurements at room temperature and low-temperature PL were used to characterize the electrical and optical properties.

2. Experimental details

Cubic GaN (c-GaN) was grown by rf-plasma-assisted MBE on semi-insulating GaAs (001) substrates [4]. C-doping of the 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 both the hole concentration and the hole mobility by Hall-effect measurements at room temperature. From the hole mobility and the hole concentration the compensation and the acceptor concentration can be estimated [18]. In GaAs:C the hole concentration versus hole mobility follows within experimental uncertainties the values cited in the literature [19]. The growth rate of GaAs was measured by reflection high-energy electron

diffraction (RHEED) oscillations. From these results it may be concluded that a maximum C-concentration of about 10^{20} cm^{-3} should be achievable in c-GaN. SIMS measurements of a C-doped c-GaN sample, where C was evaporated with the maximum e-beam evaporation power of 400 W, indeed showed an incorporated C concentration of 2×10^{20} cm^{-3}. The SIMS value is comparable, within experimental error, to the value estimated from the GaAs calibration data (1–2×10^{20} cm^{-3}) by taking into account the different growth rates.

Hall-effect measurements were performed using square-shaped samples at 300 K at a magnetic field of 0.8 T and with the samples in the dark. PL measurements were performed in a He bath cryostat between 2 and 300 K. The luminescence was excited by a cw HeCd UV laser with a power of 3 mW and was measured in a standard PL system.
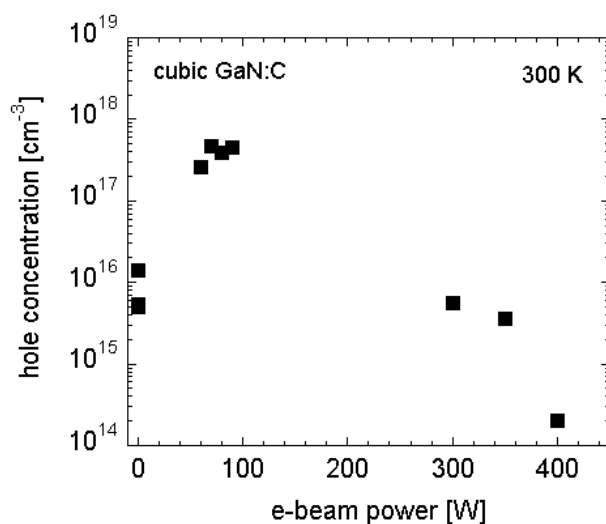
Figure 1. Room-temperature hole concentration in c-GaN measured by the Hall effect versus the power of the e-beam used to evaporate carbon from a graphite rod.

3. Results and discussion

Figure 1 shows the room-temperature hole concentration as a function of the e-beam evaporation power of C-doped c-GaN epilayers. The hole concentration increases up to a maximum value of about 6×10^{17} cm^{-3} at about 150 W. This value is approximately one order of magnitude higher than the value measured by Mg-doping of c-GaN [20] and demonstrates the ability of C for p-type doping of cubic GaN. However, above 200 W a clear reduction of the free hole concentration is seen again. This indicates that at higher C concentrations additional compensating centres are introduced into the samples.

The electrical data are supported by PL measurements. Figure 2 shows PL spectra of differently C-doped c-GaN epilayers measured at 2 K. The C-related transitions are indicated by arrows. In the near band edge region of cubic GaN a new PL band at 3.08 eV appears with increasing e-beam evaporation power, apart from the well known lines of the nominally undoped c-GaN (X and (D^0, A^0) at 3.27 and 3.16 eV, respectively [21]). From the spectral energy and the knowledge of the energy gap of c-GaN the binding energy of the C acceptor is estimated to be about $E_C = 0.215$ eV. This demonstrates that C indeed introduces a shallow acceptor in c-GaN and that the binding energy of C is about 15 meV lower than that observed for
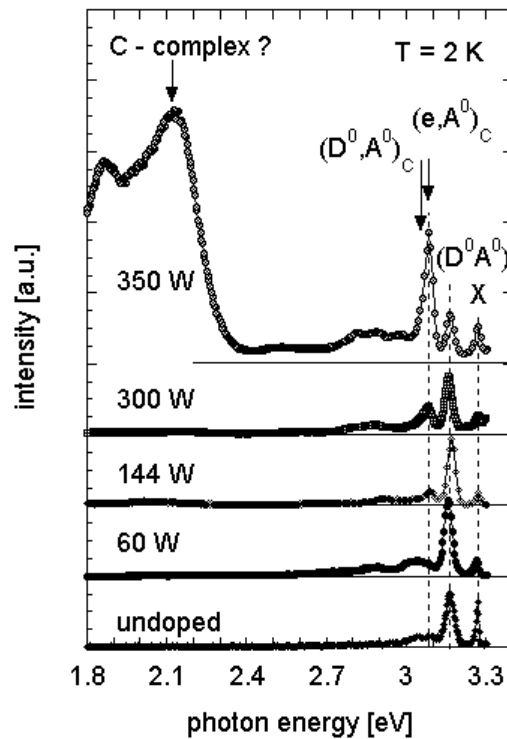
Figure 2. Low-temperature (2 K) PL spectra of different C-doped c-GaN epilayers.

the Mg acceptor in c-GaN [22]. However, at an e-beam evaporation power of 350 W PL peaks at lower energies demonstrate that at high C concentrations an additional deeper C-related defect is formed. From the energetic position of this red band (2.12 eV) we estimate a deep level positioned at about 1.185 eV below the conduction band of c-GaN. The peaks at 1.99 and 1.89 eV may be attributed to transitions from this deep level to the residual omnipresent acceptor and to the C acceptor, respectively.

In figure 3 the temperature dependence of the peak positions of the exciton and the C-related transitions at 3.08 eV are depicted. Line shape analysis of the 3.08 eV band demonstrates that this band consists of two lines separated by 25 meV. The contribution at the high-energy side becomes dominant at temperatures above 100 K. Therefore we attribute the lower transition to a donor–acceptor $(D^0, A^0)_C$ recombination, which transforms into a band–acceptor $(e, A^0)_C$ with increasing temperature. In order to separate the overlapping $(D^0, A^0)_C$ and $(e, A^0)_C$ lines in our spectra we applied a fitting procedure using two Gaussian curves with a fixed 25 meV energy separation. The peak positions of the $(D^0, A^0)_C$ and $(e, A^0)_C$ transitions are plotted in figure 3 as full squares and full circles, respectively. The uppermost full curve is the variation of the gap energy after [23]. The two full curves at the bottom are calculated for the $(e, A^0)_C$ and $(D^0, A^0)_C$ transitions, using donor and acceptor energies of 25 and 215 meV, respectively. The donor involved has the same ionization energy as the one observed in undoped samples [21]. The good agreement between the experimental data and the calculated curves supports the interpretation that in c-GaN carbon introduces a shallow acceptor with $E_A = 215$ meV. This value is lower than that for Mg_{Ga} in c-GaN [22] and is also lower than the activation energy of C measured in hexagonal GaN (230 meV) [16].
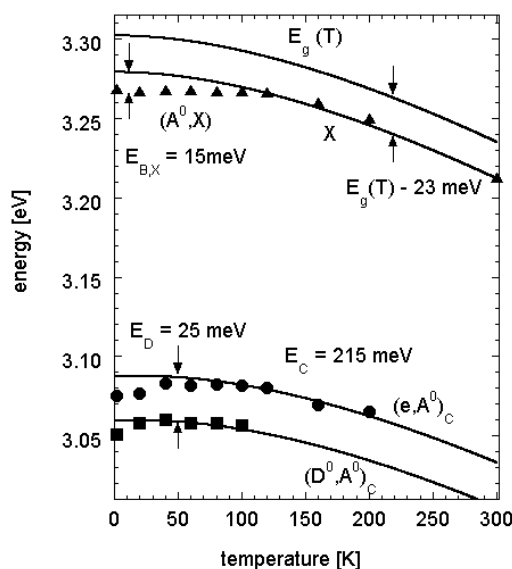
Figure 3. Temperature shift of the c-GaN near-band edge PL lines (triangles, excitonic transition; circles, C-related band–acceptor transition $(e, A^0)_C$; and squares, C-related donor–acceptor transition $(D^0, A^0)_C$). The uppermost full curve is the variation of the gap energy following [23]. The lowest full curves are calculated for $(e, A^0)_C$ and $(D^0, A^0)_C$ transitions using donor and acceptor energies of 25 and 215 meV, respectively.

Recently, Pödör [24] proposed a semiquantitative model of chemical trends in acceptor ionization energies (chemical shift) based on electronegativity differences $\Delta \chi$ between the acceptor atoms and the host atom they substitute. This semiempirical model seems to hold well for GaAs, GaP and InP. Unfortunately, this model works well only for the column II acceptors (Mg, Zn, and Cd) replacing Ga or In. For C replacing N this model predicts an $(\Delta \chi)^2$ of about 0.25, which is by far too large. Nevertheless if the acceptor binding energy of C, Mg, Zn and Cd measured in GaN is plotted versus the corresponding values measured, for example, in GaAs an excellent correlation is found, as shown in figure 4. Similar correlations are also found for the other III–V semiconductors GaP and InP (not shown here). Although the full line in figure 4 is only a guide for the eye, one clearly sees that in c-GaN the chemical trend of the estimated acceptor energy is in agreement with observations made in other III–V compound semiconductors.

The nature of the deep compensating complex has been unclear up until now. Since the PL peak intensity of the shallow C acceptor line increases with the carbon concentration, although the free hole concentration drastically decreases, we can exclude the formation of donor–acceptor nearest-neighbour pairs to explain this behaviour. The formation of nearest-neighbour pairs should significantly lower the carrier mobility since they introduce an additional scattering channel, however it should not change the concentration of conduction electrons and holes [8]. To explain the reduction in free hole concentration at the high C concentration the compensation defect has to act at least either as a double donor or as a triple donor. Therefore we propose that either a complex consisting of a C_N and a second-nearest Ga vacancy (similar to the case of Mg [1]) or a C interstitial may be responsible for the deep defect.
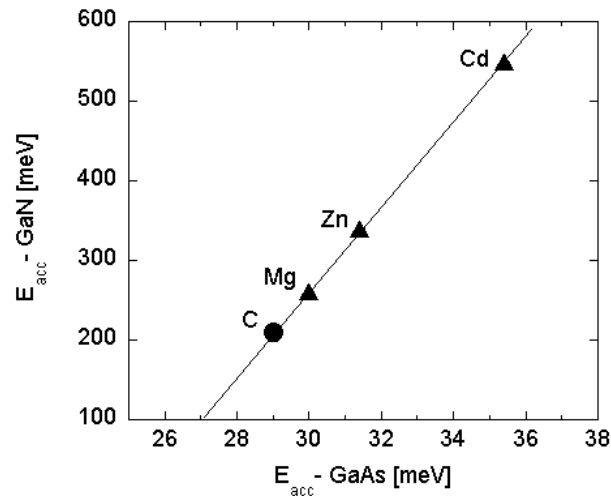
Figure 4. Acceptor binding energies of C, Mg, Zn and Cd measured in GaN versus the corresponding acceptor binding energies measured in GaAs [24]. The full line serves as a guide for the eye.

4. Conclusions

Successful p-type doping of cubic GaN epilayers using carbon has been performed by rf-plasma-assisted MBE using an e-beam evaporation source. Hall-effect measurements of our C-doped c-GaN epilayer gave hole concentrations as high as 6×10^{17} cm^{-3} and room-temperature mobilities of 200 cm^2 V^{-1} s^{-1}. Low-temperature photoluminescence showed a new line appearing at 3.08 eV with increasing e-beam evaporation power. Temperature-dependent measurements of the 3.08 eV line showed a thermalization above 100 K, which is typical for a donor acceptor (D^0A^0) transition. From the spectral energy the binding energy of the C acceptor is estimated to be about $E_C = 0.215$ eV. Our experiments demonstrate that C does indeed introduce a shallow acceptor in c-GaN and that the binding energy of C is about 15 meV lower than that observed for the Mg acceptor in c-GaN.

Acknowledgments

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