

## Optical Properties of Germanium Doped Cubic GaN

Donat J. As<sup>1</sup>, Michael Deppe<sup>1</sup>, Jürgen Gerlach<sup>2</sup> and Dirk Reuter<sup>1</sup>

<sup>1</sup>Universität Paderborn, Department Physik, Warburger Strasse 100, 33098 Paderborn, Germany

<sup>2</sup>Leibniz-Institut für Oberflächenmodifizierung (IOM) e.V., Permoserstr. 15, 04318 Leipzig, Germany

### ABSTRACT

We report on recent doping experiments of cubic GaN epilayers by Ge and investigate in detail the optical properties by photoluminescence spectroscopy. Plasma-assisted molecular beam epitaxy was used to deposit Ge-doped cubic GaN layers with nominal thicknesses of 600 nm on 3C-SiC(001)/Si(001) substrates. The Ge doping level could be varied by around six orders of magnitude by changing the Ge effusion cell temperature. A maximum free carrier concentration of  $3.7 \times 10^{20} \text{ cm}^{-3}$  was measured in the GaN layers via Hall-effect at room temperature. Low temperature photoluminescence (PL) showed a clear shift of the donor-acceptor emission to higher energies with increasing Ge-doping. Above a Ge concentration of  $\sim 2 \times 10^{18} \text{ cm}^{-3}$  the near band edge lines merge to one broad band. From temperature dependent measurements of the observed excitonic and donor-acceptor transitions a donor-energy of  $\sim 36 \text{ meV}$  could be estimated for Ge.

### INTRODUCTION

Germanium was recently introduced as a highly favorable n-type dopant in hexagonal GaN (h-GaN) [1]. In comparison to the standard Si donor, the superiority of Ge doped h-GaN is demonstrated by very high free carrier concentrations above  $10^{20} \text{ cm}^{-3}$  with smooth surfaces and reduced tensile strain [2]. However, due to symmetry reasons h-GaN, if grown in c-plane, exhibits strong spontaneous and piezoelectric polarization fields at interfaces and surfaces, which limit the recombination efficiency in e.g. double heterostructures or quantum wells. To overcome these harmful effects non-polar or semi-polar h-GaN may be grown or as an additional alternative way the metastable cubic phase of GaN (c-GaN) may be used, where these fields are absent. Therefore, for device applications it will be very attractive to investigate the behavior of Ge as an alternative n-type dopant in cubic group III-nitrides.

### EXPERIMENT

Cubic GaN (c-GaN) epilayers were grown by plasma-assisted molecular beam epitaxy (MBE) in a *Riber 32* system. 10  $\mu\text{m}$  thick 3C-SiC (001) layers, which were deposited on 500  $\mu\text{m}$  Si (001) were used as substrates [3]. Ga, Ge, and Si molecular beams were provided by effusion cells and an *Oxford Applied Research HD25* radio frequency plasma source was used to generate activated nitrogen atoms. All samples have been grown at a substrate temperature around 720 °C employing a Ga flux of  $3.4 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ .

A series of samples each consisting of a nominally 600 nm thick Ge-doped c-GaN layer was grown. The Ge effusion cell temperature was varied between 600 °C and 1000 °C in steps of 100 °C to achieve doping levels varying over several orders of magnitude. Time of flight secondary ion mass spectroscopy (ToF-SIMS) demonstrates the incorporation of Ge into c-GaN

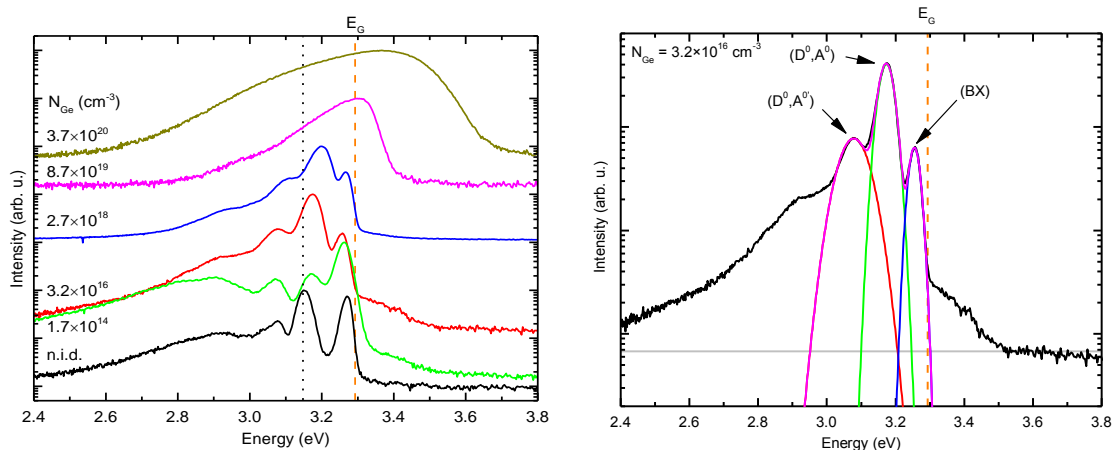
and showed that the uncalibrated incorporated Ge concentration follows the vapor pressure curve of Ge. For a Ge cell temperature of 900°C and 1000 °C Hall-effect measurements at room temperature gives a free electron concentration of  $8.7 \times 10^{19} \text{ cm}^{-3}$  and  $3.7 \times 10^{20} \text{ cm}^{-3}$  [4]. Assuming that the free carrier concentration corresponds to the actual donor concentration (degenerated case), this Hall data are used to calibrate the Ge concentration measured by ToF-SIMS.

The luminescence was excited by a Nd:YAG laser emitting at 266 nm (4.66 eV) with a power of 5 mW and measured in a standard PL system, consisting of a SPEX 270 M monochromator and a CCD array (Andor iDus 420). A closed-cycle cryostat was used to vary the sample temperatures from 13 K to room temperature.

## RESULTS AND DISCUSSION

### Photoluminescence of Ge doped cubic GaN

The optical properties of Ge doped cubic GaN at low temperature are shown in Fig.1a. At 13 K the spectrum of the not intentionally doping (n.i.d) sample and the sample with the lowest Ge concentration ( $3.2 \times 10^{16} \text{ cm}^{-3}$ ,  $T_{\text{Ge}} = 600^\circ\text{C}$ ) is dominated either by the excitonic transition X at 3.26 eV or by the donor-acceptor pair transition ( $D^0, A^0$ ) at 3.15 eV [5]. With increasing Ge doping a clear shift to higher energies of the ( $D^0, A^0$ ) is observed. In contrast to that, the transition X stays at its position as expected for an excitonic line. Beyond a Ge-concentration of  $2.7 \times 10^{18} \text{ cm}^{-3}$  ( $T_{\text{Ge}} > 800^\circ\text{C}$ ) both lines merges to one broad band and the peak maximum shifts monotonically towards higher energies with increasing Ge doping. Simultaneously the spectral shape of the main emission line becomes strongly asymmetric having a steep slope on the high-energy side and a smooth slope on the low energy side of the spectra. Such a behavior is characteristic for momentum non-conserving (non-vertical) band-to-band transitions or to recombination of free electrons to local hole states [6] and has been observed in the spectra of GaAs heavily doped with Te [6] or Si [7]. The position at the steep high energy edge of the luminescence band is determined by the electron Fermi-level and it shifts to higher energies (Burstein-Moss shift [8]) as the conduction band fills with free electrons.



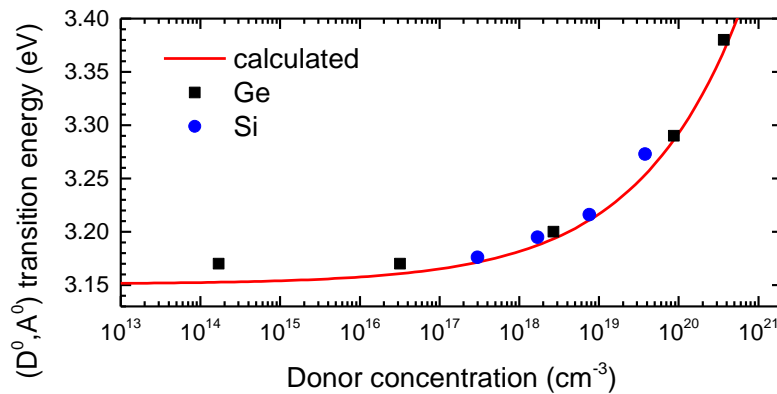
**Figure 1.** a) Photoluminescence (PL) spectra of a nominally undoped (n.i.d) sample and various Ge-doped samples measured at 13 K. The spectra are normalized and shifted vertically for better clarity. b) Gaussian functions are fitted to the PL spectrum of the  $3.2 \times 10^{16} \text{ cm}^{-3}$  Ge-doped sample. The near band edge emission consists of the recombination of bound excitons (BX) and two donor-acceptor pair transitions ( $D^0, A^0$ ) and ( $D^0, A^0$ ), respectively.

In Fig. 1b the PL spectrum of the sample doped with a Ge concentration of  $3.2 \times 10^{16} \text{ cm}^{-3}$  is depicted for a more detailed discussion. Three emission peaks dominate the spectrum and are fitted by Gaussian functions. The emission at 3.25 eV is related to the recombination of bound excitons (X) [5,9]. The most intensive peak at 3.17 eV originates from recombination of donor-acceptor pairs ( $D^0, A^0$ ) [5]. An additional donor-acceptor pair recombination ( $D^0, A^{0'}$ ) involving a second acceptor can be seen at 3.08 eV. It is assumed that C is involved as an acceptor in this transition [10]. The dashed vertical line marks band gap energy  $E_G = 3.29 \text{ eV}$  of c-GaN the 13 K [11,12].

The peak position of the ( $D^0, A^0$ ) as a function of the Ge donor concentration is plotted in Fig. 2. Using a simple Coulomb-term model [13] the peak position of the ( $D^0, A^0$ ) transition can be estimated by

$$E_{(D^0, A^0)} = E_{gap} - (E_D + E_A) + \frac{e^2}{4\pi\epsilon_0\epsilon R} \quad \text{with} \quad R = \frac{1}{2} \cdot \frac{1}{\sqrt[3]{N_{Ge}}} \quad (1)$$

The full line in Fig.2 represents the model prediction and shows an excellent agreement with the experimental data (full black squares). For comparison data of the ( $D^0, A^0$ ) transition of Si doped cubic GaN (blue dots) [14] are also included in this plot, demonstrating that both donors Ge and Si behave nearly identical in cubic GaN.



**Figure 2.** Donor-Acceptor transition energy ( $D^0, A^0$ ) at 13 K photoluminescence (PL) spectra of Ge-doped (full squares) and Si-doped (blue circle) samples. The donor concentration is calculated using the vapor pressure curve and the Hall data at high T.

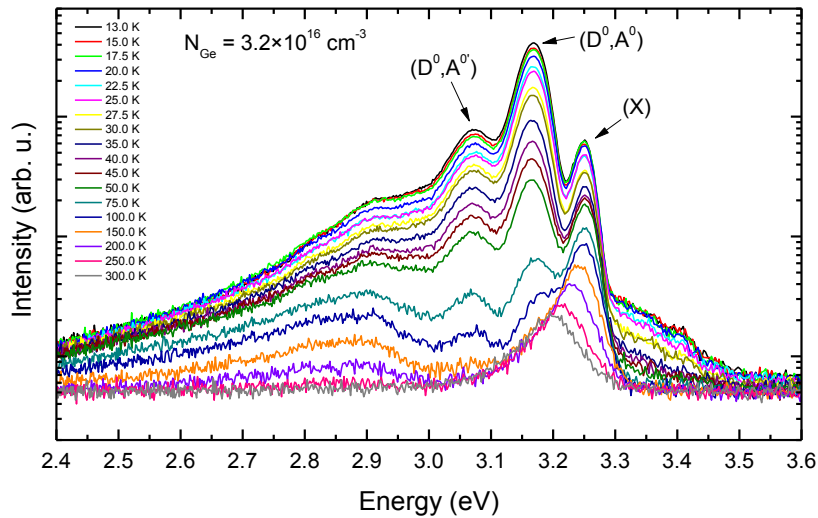
### Temperature dependence photoluminescence of Ge doped cubic GaN

Figure 3 shows the PL spectra of a cubic GaN epilayer doped with  $N_{Ge} = 3.2 \times 10^{16} \text{ cm}^{-3}$ . As described above the spectra at low temperature is dominated by an exciton transition (X) and two donor-acceptor transitions ( $D^0, A^0$ ) and ( $D^0, A^{0'}$ ). With increasing temperature the donor-acceptor transition progressively quenches to the benefit of the excitonic transition X and at room temperature only this line remains. Simultaneously above 120 K a clear redshift of the band edge luminescence can be observed.

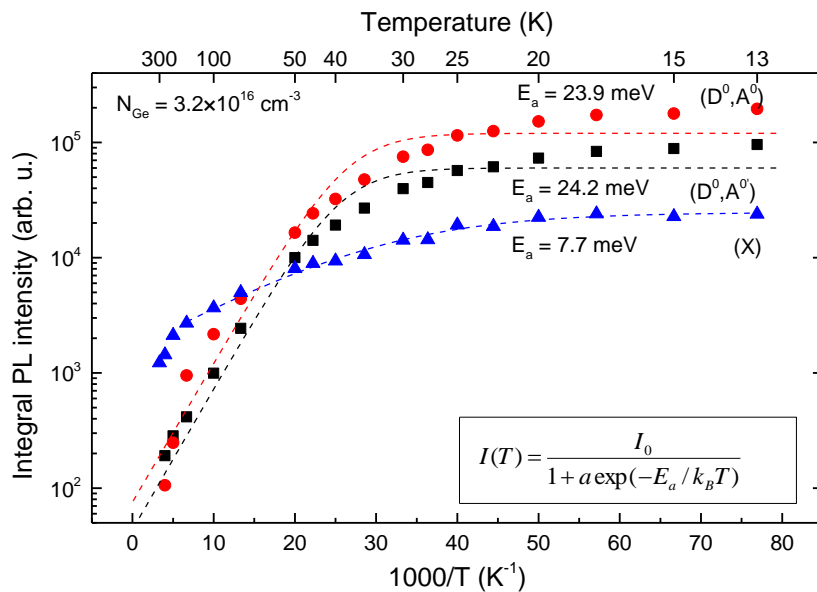
Figure 4 is an Arrhenius plot of the integrated intensities of the ( $D^0, A^0$ ), ( $D^0, A^{0'}$ ) and X lines. The intensities decrease rapidly due to thermal quenching. A single quenching mechanism is found to explain the temperature dependence. In this case the T-dependence can be written as

$$I(T) = \frac{I_0}{1 + a \cdot \exp\left(-\frac{E_a}{k_B T}\right)} \quad (2)$$

where  $I(T)$  is the integral intensity at temperature  $T$ ,  $I_0$  and  $a$  are constants,  $k_B$  is the Boltzmann's constant, and  $E_a$  is equal to the activation energy of the involved process [15]. For the  $(D^0, A^0)$  and  $(D^0, A^0)$  transitions an activation energy  $E_a$  of 23.9 meV and 24.2 meV is estimated for the involved donors, respectively.



**Figure 3.** Temperature dependence of the luminescence spectra of a cubic GaN epilayer doped with  $3.2 \times 10^{16} \text{ cm}^{-3}$  Ge atoms.



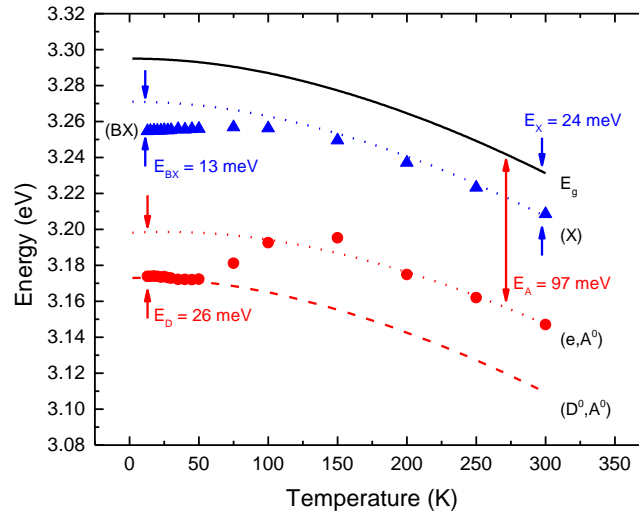
**Figure 4.** The integral intensity of the exciton (X) (blue triangles), the  $(D^0, A^0)$  (red dots) and the  $(D^0, A^0)$  (black squares) transition as a function of the reciprocal temperature.

At low temperature the excitonic line X quenches with a small activation energy  $E_a$  of about 7.7 meV. At temperatures above 200 K a second thermally activated process with an higher

activation energy of about 24 meV (not shown here) appears for the X transition. As such we interpret the first decrease of the X line to thermal detrapping towards the free exciton band. Using the empirical Haynes`rule,

$$E_{BX} = a_1 + a_2 E_D \quad (3)$$

which correlates the localization energy of the exciton  $E_{BX}$  and the donor binding energy  $E_D$ , the donor binding energy can be calculated [16,17]. With  $a_1=0$  and  $a_2=0.214$  for GaN [18] a binding energy of  $E_{Ge}=36$  meV can be estimated. This donor binding energy is in excellent agreement with early results on Ge doped hexagonal GaN grown by MOCVD (34 meV) [19] and with theoretical calculations (30 meV) [20].



**Figure 5.** Temperature shift of the Ge doped c-GaN near band edge PL-lines (blue triangles excitonic transition (X), red dots ( $D^0, A^0$ ) and ( $e, A^0$ ) transitions).

In Figure 5 the temperature shift of the 3.26 eV line (X) (blue full triangles), the band acceptor transition ( $e, A^0$ ) and the ( $D^0, A^0$ ) transition (full dots) are plotted versus temperature. The dotted blue curve represents the temperature dependence of the free exciton transition as measured with photo-reflectivity (PR) by Feneberg et al. [11]. As expected the PL peak overlaps with the exciton transition from PR at elevated temperatures, while at low temperatures a difference between PL and PR of about 13 meV due to localization of the excitons to donors is observed. The difference in binding energy of the bound exciton estimated from the Arrhenius plot (see Fig.4) and this energy shift (see Fig.5) is unclear up to now. The temperature dependence band gap energy of cubic GaN is also plotted as full black curve in Fig. 5 by adding the free exciton binding energy of  $E_x = 24$  meV to the free exciton curve [11].

Considering the separation between the ( $D^0, A^0$ ) and ( $e, A^0$ ) peaks (26meV) and accounting the effective Coulomb interaction in ( $D^0, A^0$ ) (about 9.68 meV for  $N_{Ge}=3.2 \times 10^{16} \text{cm}^{-3}$ ), we estimate the ionization energy of the shallow Ge donor as  $E_D=36$  meV, in excellent agreement with the value determined from the exciton localization energy. The involved acceptor has a depth of about 97 meV. The binding energy of Ge is slightly higher than that for the Si [5].

## CONCLUSIONS

Plasma-assisted molecular beam epitaxy was used to deposit Ge-doped cubic GaN layers. The Ge doping level was varied by around six orders of magnitude by changing the Ge effusion

cell temperature. SIMS measurements verify the incorporation of Ge in cubic GaN and with Hall-effect measurements a maximum free carrier concentration of  $3.7 \times 10^{20} \text{ cm}^{-3}$  was determined. Low temperature PL showed a clear shift of the donor-acceptor emission to higher energies with increasing Ge-doping. At high Ge concentration of the near band edge lines merge to one broad band. From temperature dependent measurements of the observed donor bound exciton transition and the donor-acceptor transition a donor-energy of  $\sim 36 \text{ meV}$  could be estimated for Ge.

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