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# N-type doping of HVPE-grown GaN using dichlorosilane

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N-type doping of GaN in hydride vapour phase epitaxy (HVPE) has been studied. While silane was found to be not suitable, doping from solid silicon was found to be feasible but difficult to handle. Dichlorosilane was found to be a convenient Si doping source for HVPE growth of GaN. High electron mobilities as well as good optical and structural properties are obtained in the doping range of $6 \times 10^{17}$ cm$^{-3}$ to $8 \times 10^{18}$ cm$^{-3}$ using dichlorosilane.



## 1 Introduction

Hydride vapour phase epitaxy (HVPE) has widely been accepted to be the most promising technique for the growth of freestanding GaN substrates for device application. For LEDs and laser diodes n-type doping of the GaN template or substrate is desired since this allows for the vertical design with front and backside contacts known from GaAs- and InP-technology. Silane was reported to be a suitable source for doping up to $5 \times 10^{18}$ cm$^{-3}$ in a first report on intentional *n*-doping of HVPE-grown GaN [1]. Later, another method using a solid Si-source exposed to HCl to form $SiCl_x$ was reported [2]. By variation of the Si source temperature between 200 and 500 °C a free electron concentration up to $8 \times 10^{18}$ cm$^{-3}$ was achieved with an electrical activation of 30–50%. In this paper after a brief discussion of the above doping methods gaseous dichlorosilane is shown to be a more convenient source for intentional *n*-doping of HVPE-grown GaN with good electrical, optical and structural properties.

## 2 Experimental

HVPE growth was performed in an horizontal AIX-HVPE reactor described in [3]. Disilane ($Si_2H_6$), pieces of silicon wafers (Si) exposed to HCl at about 850 °C, and finally dichlorosilane ($SiH_2Cl_2$) were examined to achieve *n*-doping of GaN layers. $SiH_2Cl_2$ was added either via a showerhead directly to the substrate or into the main $N_2/H_2$ carrier gas. For the latter case, series of GaN layers with variation of the $SiH_2Cl_2$ flow from 0 to 25 sccm were grown at total pressures of 800 and 200 hPa. The growth temperature of 1040 °C, the flows of 500 sccm for $NH_3$ and 60 sccm for HCl passing the metallic Ga were kept konstant. GaN layers of 2.5 µm thickness and high sheet resistance (>400 kΩ/sq) grown by MOVPE on (0001) sapphire were used. The thicknesses of the HVPE-grown GaN layers which ranged from 2.5 µm to 3 µm for dopant flows below 25 sccm were determined gravimetrically. Normarski microscopy, Hall effect, SIMS, PL and HRXRD measurements were used to assess the layer properties.

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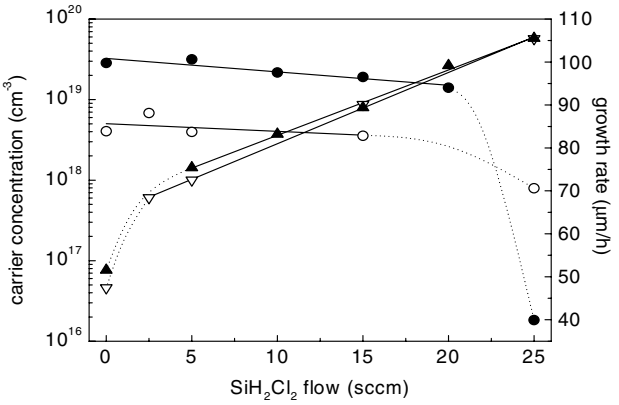


**Fig. 1** Free carrier concentration (▲: 800 hPa, ▽: 200 hPa) and growth rate (●: 800 hPa, ○: 200 hPa) vs. $SiH_2Cl_2$ flow rate (lines are guides for eyes only).

## 3 Results and discussion

The injection of $Si_2H_6$ which is standardly used for *n*-doping of GaN in our MOVPE into the HVPE reactor resulted in a colored deposition at the quartz wall at the entrance into the heated region. No Si in the GaN layers could be detected by SIMS. $SiH_4$ and $Si_2H_6$ decay rapidly at temperatures below the 850 to 900 °C used for the Ga source [4]. Thus, silanes were found to be too instable in this hot wall reactor geometry where the doping gas has to pass along the hot Ga source region before reaching the substrate. Solid Si exposed to HCl by substitution of a metallic Ga source was found to work although the Si source temperature of 900 °C was higher than that reported in [2]. But the exposed Si surface was found to change with operation time in area and morphology resulting in difficulties in controllability. Moreover, the solid Si occupied one source place usually used for Ga. Therefore, this method was discarded. However, the chemistry behind it was found to be interesting. It is based on the formation of chlorinated silanes most probably due to the reaction $Si + 3HCl \Rightarrow SiHCl_3 + H_2$ which takes place at temperatures above 300 °C [5]. At high temperatures preferentially in the presence of $H_2$ [5] it decays in the gas phase into $SiCl_2$ and HCl. Subsequently, $SiCl_2$ decomposes at free surface sites to Cl* and SiCl* and further with H* to 2HCl* and Si* [4]. SiCl* being similar to GaCl* is thought to drive Si atoms onto Ga sites in GaN. Hence, the analysis of the reaction mechanism for doping from solid Si suggests to directly use chlorosilanes. Due to the higher thermal stability chlorosilanes should suffer less from the premature decomposition found for silanes. Based on the analysis of available thermo-chemical data [4] and the availability in high purity but small quantity $SiH_2Cl_2$ was chosen as the most promising candidate. $SiH_2Cl_2$ is an easily available standard precursor with a vapour pressure of 1.6 bar (20 °C). It decomposes heterogeneously to SiCl* at high temperatures and offers a high Si : Cl ratio. Thus, $SiH_2Cl_2$ was added to the main $N_2/H_2$ carrier gas resulting in doped GaN layers with a uniform morphology across the wafer. The carrier concentrations and the growth rates obtained are shown in Fig. 1. The free carrier concentrations for $SiH_2Cl_2$ flow rates from 5 to 25 sccm increase linearly in a semilog-plot from about $6 \times 10^{17}$ cm$^{-3}$ to $6 \times 10^{19}$ cm$^{-3}$ at total pressures of 800 and 200 hPa. The growth rates slightly decrease with the addition of $SiH_2Cl_2$ up to about 15 sccm from 100 µm/h with −0.31 µm/h sccm at 800 hPa and from 85 µm/h with a lower slope of −0.17 µm/h sccm at 200 hPa. Above a flow of 20 sccm of $SiH_2Cl_2$ the growth rate breaks down in particular at 800 hPa accompained by a rough surface morphology typical for etched surfaces as shown in the optical micrographs in Fig. 2b and d. The observed growth rate breakdown can not be explained by the formation of HCl alone because the addition of 50 sccm HCl to the carrier gas without $SiH_2Cl_2$ did not show a comparable effect on the morphology and growth rate. The surface morphology remained unchanged for $SiH_2Cl_2$ flows up to 15 sccm as shown in Fig. 2a and c. Figure 3 shows the electron mobility against the carrier concentration. The mobility for intentionally Si-doped samples is in a reasonable range of mobility for carrier concentrations between $6 \times 10^{17}$ cm$^{-3}$ and $8 \times 10^{18}$ m$^{-3}$ [6].

 

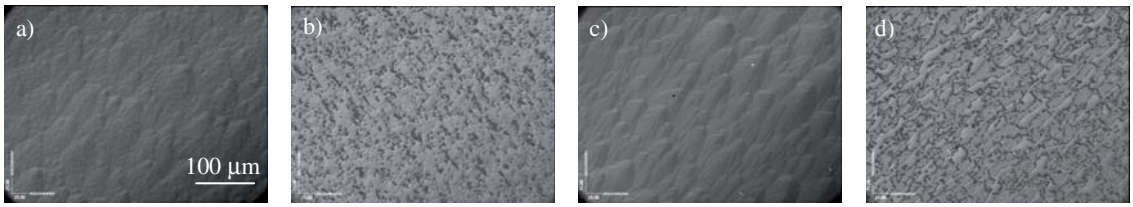


**Fig. 2** Optical micrographs of Si-doped GaN layers grown at 800 hPa with 15 sccm (a) and 25 sccm (b), and at 200 hPa with 15 sccm (c) and 25 sccm (d) of $SiH_2Cl_2$.

Thus under the used growth conditions $SiH_2Cl_2$ flows up to 15 sccm can be used yielding n-type doping up to $8 \times 10^{18}$ cm$^{-3}$ with smooth surfaces. Since at 800 hPa a higher growth efficiency is obtained than at 200 hPa the discussion of the structural properties of the GaN layers is focussed on the higher growth pressure. PL spectra recorded at 300 K (Fig. 4) reveal a higher intensity of the near-band-edge transitions and phonon replica at lower energy for the sample doped with 15 sccm $SiH_2Cl_2$ in comparison to an undoped layer. Yellow luminescence was not observed. A small red-shift of 4 meV and linewidth broadening from 19 meV to 22 meV is observed for the doped sample. Both values are much lower than values reported for MOVPE-grown GaN layers doped with silane [7] where the broadening was explained by concentration fluctuations. The red-shift is thought to originate from reduced biaxial compressive strain due to increased biaxial tensile strain caused by Si-incorporation [8, 9]. This finding is also supported by the determination of the lattice constant $c$ and the resulting strain $\varepsilon_{zz}$ from $2\theta$ X-ray scans at the (0002) reflection shown in Table 1 where both $c$ and $\varepsilon_{zz}$ decrease with increasing Si doping. Again, the intrinsically incorporated tensile strain found here is lower than that reported for Si-doped GaN grown by MOVPE [10]. These differences indicate a lower concentration of intrinsic defects in case of Si-doping with $SiH_2Cl_2$ in HVPE-grown GaN layers. In addition, X-ray data from $\omega$-scans in Table 1 show that the structural crystal quality is not affected by doping. The densities of edge and screw dislocations at the surface can be estimated after [11] from the FWHM of $\omega$-scans at the (0002) and the $(30\bar{3}2)$ reflections. The resulting total dislocation density of $5 \times 10^9$ cm$^{-2}$ is primarily due to edge dislocations.

Comparison of Hall effect and SIMS data given in Table 1 shows that the electrical activation $n$/[Si] for the Si-doped GaN layers is not complete. Nevertheless, the activation of above 50% is higher than that published for doping with solid Si in HVPE [2]. It did not change after annealing in $N_2$ atmosphere at 730 °C for 20 min. The oxygen content [O] determined by SIMS was about $2 \times 10^{17}$ cm$^{-3}$ for all samples of Table 1 independent of the $SiH_2Cl_2$ flow rate. Thus neither passivation nor an additional uptake of oxygen due to the use of $SiH_2Cl_2$ was observed. It is interesting to note that a higher activation of Si was observed in one of our preliminary growth experiments in which simply the solid Si was removed and $SiH_2Cl_2$ was injected instead of HCl into the $N_2$ flow through the showerhead. While in this case the outer regions of the wafer revealed a rough surface it was smooth in an inner circle of about 2 cm in diameter where the GaCl and SiCl* streams mix effectively. Due to this inhomogeneity, this approach was discarded. However, the activation of Si in this sample grown with a different injection scheme was

**Table 1** Silicon [Si] content from SIMS, carrier concentration $n$ and mobility $\mu$ from Hall effect, activation ratio $n$/[Si], lattice constant $c$, strain $\varepsilon_{zz}$ ($c_0$ = 5.1851 Å was used) and FWHM in X-ray ($\omega$ scan) of samples with smooth surface morphology grown at 800 hPa.

| $SiH_2Cl_2$ (sccm) | [Si] (cm$^{-3}$) | N (295 K) (cm$^{-3}$) | $\mu$ (295 K) (cm$^2$/Vs) | $n$/[Si] (%) | $c$ (Å) | $\varepsilon_{zz}$ (%) | FWHM (0002) (arcsec) | FWHM $(30\bar{3}2)$ (arcsec) |
|---|---|---|---|---|---|---|---|---|
| 0 | $4.8 \times 10^{16}$ | $7.6 \times 10^{16}$ | 420 | – | 5.18628 | 0.0227 | 305 | 867 |
| 5 | $2.4 \times 10^{18}$ | $1.4 \times 10^{18}$ | 320 | 59 | 5.18620 | 0.0212 | 313 | 823 |
| 10 | $6.8 \times 10^{18}$ | $3.7 \times 10^{18}$ | 250 | 55 | 5.18617 | 0.0206 | 335 | 832 |
| 15 | $1.5 \times 10^{19}$ | $8.0 \times 10^{18}$ | 210 | 52 | 5.18581 | 0.0137 | 330 | 828 |

 

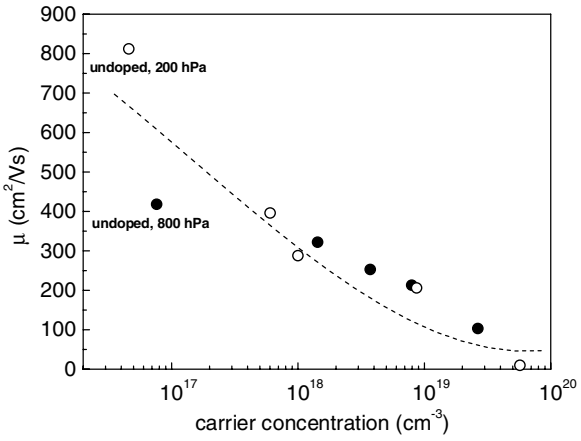


**Fig. 3** Mobility vs. carrier concentration (●: 800 Pa, ○: 200 hPa). The dashed line is fit to a number of unintentionally doped GaN layers from the same reactor.

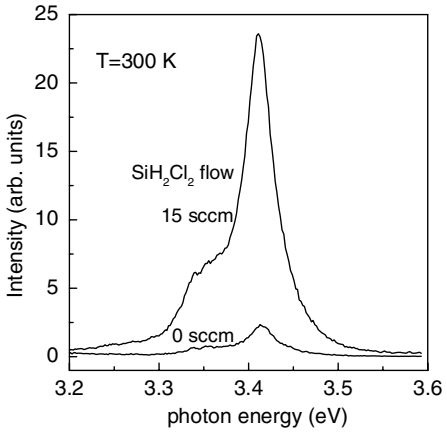


**Fig. 4** PL spectra at room temperature of GaN samples with 0 sccm and 15 sccm $SiH_2Cl_2$ flow grown at 800 hPa.

complete, i.e. [Si] = $n = 1 \pm 0.1 \times 10^{18}$ cm$^{-3}$ with a mobility of 310 cm$^2$/Vs. This finding indicates that prereactions, e.g. a partial decomposition of $SiH_2Cl_2$ in the gas phase due to the presence of $H_2$, may occur. This assumption is also supported by the minor growth rate reduction at lower reactor pressure shown in Fig. 1 since the residence time of $SiH_2Cl_2$ is reduced by the higher gas velocity. Prereactions may lead to higher fractions of H* radicals at the growth surface which may etch the surface and higher fractions of Si* radicals which may not be incorporated on Ga sites. Although the understanding of the effect of such prereactions on the level of activation needs to be improved, $SiH_2Cl_2$ is a suitable precursor for n-type doping of HVPE-grown GaN.

## 4 Conclusion

Dichlorosilane has been established as an efficient gaseous *n*-dopant precursor for the HVPE growth of GaN. While disilane is unsuitable due to predecomposition, the use of solid silicon together with hydrogen chloride works but is not very convenient. $SiH_2Cl_2$ yields layers with high electron mobilities, high PL intensity and smooth surfaces up to $8 \times 10^{18}$ cm$^{-3}$. Structural properties as revealed by X-ray diffraction remain mainly unchanged by this Si doping. The level of activation is dependent on the injection scheme pointing to the importance of prereactions for the Si incorporation site. For injection into the carrier gas above 50% activation is achieved. In summary, dichlorosilane is a well suited n-type dopant source for GaN HVPE yielding high layer quality.

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## References

[1] R. P. Vaudo and V. M. Phanse, Abstract book, MRS Fall meeting, D16.3 (1997).
[2] A. V. Fomin, A. E. Nikolaev, I. P. Nikitina, A. S. Zubrilov, M. G. Mynbaeva, N. I. Kuznetsov, A. P. Kovarsky, B. Ja. Ber, and D. V. Tsvetkov, phys. stat. sol. (a) **188**, 433 (2001).
[3] E. Richter, Ch. Hennig, M. Weyers, F. Habel, J.-D. Tsay, W.-Y. Liu, P. Brückner, F. Scholz, Yu. Makarov, A. Segal, and J. Kaeppeler, J. Cryst. Growth **277**, 6 (2005).
[4] G. Valente, C. Cavallotti, M. Masi, and S. Carr, J. Cryst. Growth **230**, 247 (2001).
[5] U. Hilleringmann, Siliziumtechnologie (Teubener Verlag, Stuttgart, 1996).

 

[6] M. N. Gurusinghe and T. G. Anderson, Phys. Rev. B **67**, 235208 (2003).
[7] E. F. Schubert, I. D. Goepfert, W. Grieshaber, and J. M. Redwing, Appl. Phys. Lett. **71**, 921 (1997).
[8] A. Shikanai, T. Azuhata, T. Sota, S. Chichibu, A. Kuramata, K. Horino, and S. Nakamura, J. Appl. Phys. **81**, 417 (1997).
[9] G. S. Sudhir, Y. Peyrot, J. Krüger, Y. Kim, R. Klockenbrink, C. Kisielowski, M. D. Rubin, and E. R. Weber, Mater. Res. Soc. Symp. Proc. **482**, 525 (1998).
[10] L. T. Romano, C. G. Van de Walle, J. W. Ager III, W. Götz, and R. S. Kern, J. Appl. Phys. **87**, 7745 (2000).
[11] T. Böttcher, Ph.D. thesis, University of Bremen (2002).

 