Si-doped GaN by Hydride-Vapour-Phase-Epitaxy Using a Ga:Si-Solution as Doping Source

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The Si-doping of GaN by hydride vapour phase epitaxy (HVPE) has been analyzed. To this end, a Ga:Si-solution was employed as Si source. Doping concentrations of up to $9 \cdot 10^{18}\,cm^{-3}$ *could be achieved. By using a second pure Ga-source, a systematic variation of the doping level was possible. Although there is a high tendency to cracking in Si-doped GaN, a layer-thickness of more than* $10\,\mu m$ *could be achieved by the insertion of a SiN-interlayer in the MOVPE-grown templates.*

1. Introduction

Currently the epitaxy of GaN-based devices has to be done on foreign substrates, such as sapphire or SiC. A high defect density arises in these devices, because of the high lattice mismatch of the foreign materials compared to GaN, which limits the overall device performance regarding efficiency and lifetime [1]. Although there are a lot of efforts using techniques like ELO or SiN-interlayer [2] to reduce the defect density during the heteroepitaxy, only homoepitaxial growth can overcome this problem and improves the defect situation drastically. For the production of the finally needed free-standing GaN-substrates the hydride vapour phase epitaxy seems to be the most promising way besides other approaches like growth from solution or supercritical ammonia. Additionally, for the production of optoelectronic devices like LEDs and laser-diodes, n-doped GaN-substrates are desired, in order to realize backside-contacts. Therefore we investigated the Si-doping during the HVPE process for future free-standing n-doped GaN-substrates.

There are a lot of possibilities for the choice of the Si doping source in HVPE. First, like commonly used in MOVPE, gaseous sources such as SiH_4 may be considered. However, SiH_4 exhibits a strong thermal instability and decays rapidly in the HVPE process before arriving at the substrate. Therefore it has to be discarded. Alternatively, chlorosilanes may be used, because of their higher thermal stability. Doping of GaN with HVPE and SiH_2Cl_2 was achieved with good material quality [3]. Another approach, which makes the additional gas-channel dispensable, is the use of solid Si, which forms $SiHCl_3$ when exposed to the HCl stream. At high temperatures, it decays into $SiCl_2$ which is then transported to the growth zone. Due to changes in the morphology of the used Si-piece, this method is difficult in controllability and reproducibility [3] [4]. To avoid this problem, we solved a piece of Si in a Ga bath and used it as Ga and Si source simultaneously.

2. Experimental

All growth experiments were done in a commercial Aixtron single-wafer HVPE system with a horizontal quartz-tube, heated in a furnace with five zones. Nitrogen was used as carrier-gas while H_2 was also added into the reactor for the reduction of cracking [5]. As nitrogen precursor, ammonia was applied, while for the group-III element a liquid Ga-bath was arranged in a HCl-stream, so that the formation of GaCl occurred and was directly injected above the substrate. In our system, two identical channels of this type were available. The substrate temperature was adjusted to 1050° C while the Ga-sources were kept at 850° C. The reactor-pressure was set to 900 mbar during these experiments.

In one of the two available source channels, 1 g Si was solved in 200 g Ga, corresponding to a molar fraction of 2.4 %. The second source channel contained a pure Ga source. Growth could be done with either one of the channels or both in combination.

The doping concentration was measured by secondary ion mass spectroscopy (SIMS) for the highest doped samples and by room-temperature Hall measurements. The crystal quality was analyzed by high-resolution x-ray diffraction (HRXRD) and by low temperature ($T = 4\,\mathrm{K}$) photoluminescence (PL).

For these studies, we used GaN templates grown in an Aixtron 200/4 RF-S system on (0001) sapphire substrates with a slight misorientation to the a-plane [6]. For the growth of the templates, an AlN nucleation layer was deposited at a temperature of 900° C and covered with a GaN-layer of about 1.6 µm. In some templates, a SiN-interlayer was deposited after the nucleation and a thin GaN-buffer.

3. Results and Discussion

First attempts where the HVPE growth was only done with the Ga:Si solution channel led to a partly passivated template due to the unintentional deposition of a thin SiN layer obviously blocking the further GaN-growth. Only the growth of some GaN islands happened, but no closed layer could be achieved (Fig. 1).

We suppose that the Ga:Si solution develops a very high Si concentration on the surface during heat-up of the reactor. When switching on the HCl gas flow, mainly SiCl is formed instead of otherwise dominating GaCl which then leads to the strong SiN deposition on the wafer. After short time (about one minute), the high Si concentration is removed from the source surface by the flowing HCl. However, owing to the partial masking of the surface by SiN only GaN islands can develop. Unfortunately, a prerun of HCl over the source without insertion of the formed SiCl into the reactor is not possible in our system.

By starting the growth with the second pure Ga source channel and then ramping over to the other channel, this problem could be solved allowing the growth of closed GaN layers.

Using only the doping channel for the main growth, samples with a doping concentration up to $9 \cdot 10^{18}\,\mathrm{cm}^{-3}$, as measured by SIMS, could be achieved. Room-temperature Hall-measurements showed also carrier-concentrations of $9 \cdot 10^{18}\,\mathrm{cm}^{-3}$ with a mobility of $167\,\mathrm{cm}^2/\mathrm{Vs}$. Obviously complete electrical activation of the incorporated Si could be achieved.

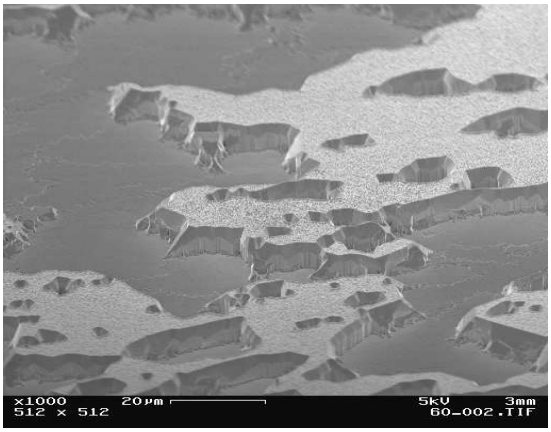

Fig. 1: SEM picture of the partly passivated surface, if growth is started directly with the doping channel.

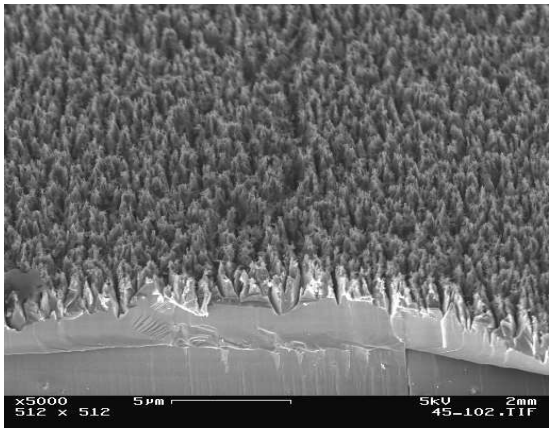

Fig. 2: SEM picture of the etched surface due to the reduction of the V/III-ratio at the growth end.

In these experiments, we discovered a decrease of the growth-rate by a factor of about 5 as compared to undoped growth. Although this reduction may be partly caused by the slightly different position of our doping shower head with respect to the substrate, we suppose that at least a factor of 4 is caused by a reduced efficiency of the GaCl formation on the Ga:Si solution.

The x-ray rocking curve of the (0002) reflection exhibits only a comparably small broadening from 217 arcsec to 277 arcsec from undoped to the doped sample (Fig. 3). Similarly, the low temperature donour-bound exciton PL peak broadened from 1.6 meV to 6.3 meV (Fig. 4). On our standard templates, the sample thickness was limited to about 10 µm, because for higher thicknesses the appearance of cracks was discovered with increasing density. Such behaviour is typical for highly Si-doped layers [7]. Such cracking could be drastically reduced by using MOVPE-templates containing a SiN-interlayer, as described in section 2.. These templates have stronger compressive strain on the surface reducing the probability of crack-formation substantially, not only for undoped growth, but also in the case of Si-doping.

3.1 Surface morphology

For optimization of the surface morphology, we have developed a 2-step growth procedure for undoped layers [8]. This process is mainly characterized by a reduction of the V/III-ratio and the pressure for the growth of the last few micrometers. Adopting this to the growth with the Ga:Si solution yielded in a rough, etched surface, as it is shown in Fig. 2. Therefore this procedure had to be skipped for the Si-doped growth.

3.2 Variable doping concentration

In order to vary the doping concentration, the HCl-flow was split between the two growth-channels with a variable ratio, while the total HCl flow was kept constant. This method

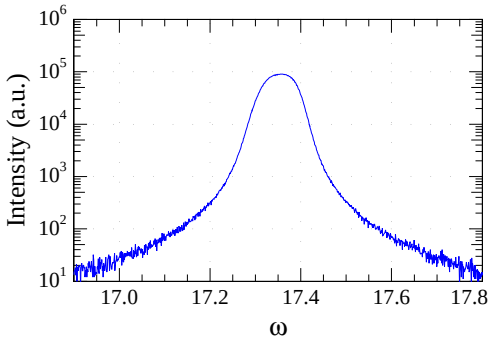

Fig. 3: HRXRD-measurement of (0002) reflection of the highly doped sample.

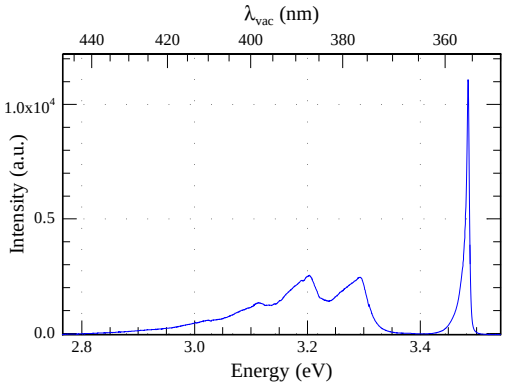

Fig. 4: Low-temperature PL-spectrum of the highly doped sample with a carrier density of $9 \cdot 10^{18}\,\mathrm{cm}^{-3}$

allowed the adjustment of the doping level from $5 \cdot 10^{16}\,\mathrm{cm}^{-3}$ to $9 \cdot 10^{18}\,\mathrm{cm}^{-3}$, while the mobility decreased from 600 to $180\,\mathrm{cm}^2/\mathrm{Vs}$. Moreover a continuous decrease in the growth rate with increasing doping concentration was found. Figure 5 shows the doping concentration and the mobility as a function of the fraction of the HCl flow in the doping channel. Low temperature PL-measurements showed a broadening of the FWHM of the D^0X-peak and a shift of its energy with increasing doping-concentration, see Fig. 6 confirming the increasing tensile strain induced by the Si doping.

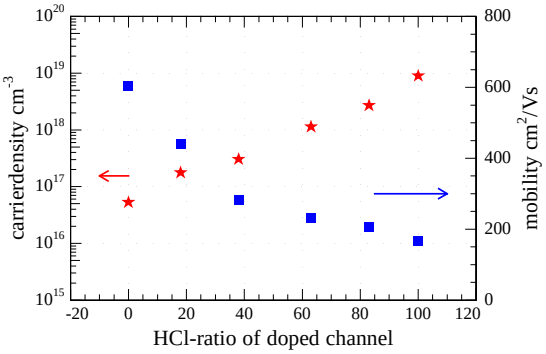

Fig. 5: Carrier-concentration (stars) and mobility vs. ratio of HCl-flow in percent through doped and undoped showerhead.

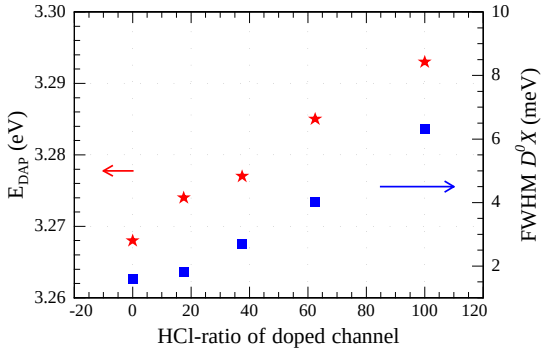

Fig. 6: Low-temperature (4 K) PL-measurements. Position of the donor-bound-exciton peak (stars) and its FWHM.

3.3 Homogeneity

The experiments with variable doping concentrations also revealed a specific problem of the used reactor geometry: Owing to the slightly different alignment of the two source channels, an inhomogenous radial doping profile develops. Furthermore, as a consequence of the high growth rate in HVPE and the comparably low rotation speed of the substrate,

the samples end up with a doping modulation profile in growth direction due to the locally periodic supply of undoped and doped source gases. These difficulties must be taken into account, if growth with varied doping level and only one Ga:Si source with constant Si fraction is desired.

3.4 Stability of the source

While the doping-source was stable during the executed growth experiments, it showed a slow decomposition with high Si-concentrations on the surface. This required already, that the growth start had to be down with the undoped channel and then ramped to the other. The possibility of further decomposition can not be neglected.

4. Conclusion

We have investigated a new doping-source for Si-doping in the HVPE. The use of a Ga:Si solution is a simple approach and we achieved doping concentrations up to $9 \cdot 10^{18}\,\mathrm{cm}^{-3}$. The samples showed fairly good quality with a FWHM of the (0002)-reflection in HRXRD of 277 arcsec and of the D^0X-peak in PL of 6.3 meV. The stability of the source was acceptable for the experimental series of some weeks, but showed already a small decomposition. The behaviour with longer operation time with many heat-up and cool-down cycles is still questionable. With the presented source-type, a variation of the doping-concentration is also possible, requiring however a well adjusted reactor geometry for a homogeneous doping profile.

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