Iron Doping in Hydride Vapor Phase Epitaxy of GaN

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In order to overcome problems with non-uniform iron (Fe) doping in our GaN layers grown by hydride vapor phase epitaxy, we have optimized the construction of our ferrocene doping channel. By pre-heating the hydrogen carrier gas before entering the hot bubbler, a constant Fe supply could be established. Moreover, losses of the precursor gas in the reactor could be minimized by a re-design of the ferrocene mini-showerhead. In consequence, an about 1 mm thick free-standing GaN layer containing a uniform Fe concentration of $2 \cdot 10^{18}$ *cm*$^{-3}$ *exhibited a specific resistivity of* $10^7\,\Omega$*cm at room temperature.*

1. Introduction

Although GaN-based heterostructures have enabled the realization of many modern semiconductor devices like high-brightness blue and green LEDs, laser diodes, and high-power high-frequency field effect transistors, there are still many issues to be optimized for such devices. Most work is still done on foreign substrates like sapphire or SiC, which leads to fairly large defect densities in the epitaxial structures. Homoepitaxial growth on GaN wafers would be preferable, however, the availability of such substrates is still very limited. Therefore, our studies concentrate since several years on the growth of thick GaN layers by hydride vapor phase epitaxy (HVPE; see, e.g., our previous Annual Reports). Particularly, we are investigating the possibilities to realize semi-insulating GaN layers by iron doping in HVPE [1]. In order to improve the doping concentration control, we have attached a metalorganic gas channel to our HVPE system enabling to supply ferrocene (bis-cyclopentadienyl-iron, Cp_2Fe) as Fe source. However, first experiments resulted in a very non-uniform doping profile with a large Fe peak after switching on the precursor channel, while the remaining layer contained nearly about an order of magnitude less [Fe] [1]. Hence, the average Fe concentration in our layer of about $1\text{–}2 \cdot 10^{17}\,\mathrm{cm}^{-3}$ was too small to compensate the parasitic background doping and to lead to semi-insulating behavior of our GaN layers. This required a redesign of our precursor channel, which will be described in this report along with the obtained results.

2. Experimental

These studies have been performed in our horizontal HVPE reactor, which contains 5 separated heating zones. Liquid Ga, positioned in zone II at a temperature of 850 °C, is transported by HCl to the substrate in heating zone IV, where the epitaxial growth takes place at typical temperatures of 1050 °C. Ammonia (NH_3) is used as nitrogen precursor. As described in our last report, the ferrocene is transported by H_2 from its bubbler into an additional quartz tube in the center of our reactor close to the growth zone. Owing to the high ferrocene bubbler temperature (see below), all gas lines connecting the bubbler and the HVPE reactor were heated by heating tapes to temperatures above 95 °C. As ferrocene would get lost by decomposing in the hot environment of our HVPE reactor, we mix it with HCl inside zone I of the HVPE reactor near to the reactor inlet to form $FeCl_2$ which then can be transported forward to the substrate. Details of this construction are described in [1].

The grown layers have been evaluated — besides standard characterization — by van der Pauw Hall experiments. In some samples, the Fe concentration has been directly determined by secondary ion mass spectrometry (SIMS), performed by Lutz Kirste *et al.* (Fraunhofer Institute of Solid State Physics, Freiburg).

3. Optimization of Doping Channel

3.1 Pre-heating of carrier gas

As mentioned above, when switching on our Fe precursor channel gas flow in our previous experiments, we had observed a peak Fe doping of up to $2 \cdot 10^{19}\,\mathrm{cm}^{-3}$ which then decreased rapidly to an average value of $1\text{–}2 \cdot 10^{17}\,\mathrm{cm}^{-3}$. Due to the very low vapor pressure of ferrocene, such values only could be obtained for bubbler temperatures of 95 °C. However, according to our conventional metalorganic precursor channel construction, the ferrocene bubbler was flushed with "cool" H_2 of about 20 °C (room temperature). Moreover, it must be considered that ferrocene is still solid even at 95 °C. Therefore, we tentatively explain the observed doping peak by a transportation of a large amount of ferrocene according to its vapor pressure at 95 °C only in the very first moment. However, then the "cool" H_2 carrier gas locally decreases the ferrocene temperature and also its vapor pressure. This leads to a reduced ferrocene uptake, keeping in mind a fairly low thermal conductivity of the solid ferrocene, whereas in a liquid material, the carrier gas bubbling would lead to a mixing of the material and hence to a much weaker temperature gradient.

Therefore, it is obvious that a pre-heating of the H_2 carrier gas would decrease our problem. We connected a coil of several windings of our H_2 precursor supply line connected to the inlet of the ferrocene bubbler, which was immersed into the thermo-bath liquid of our ferrocene bubbler. At a typical flow of 40 sccm, the carrier gas needs about 20 s to flow through this coil, which should be enough to heat up to the bubbler temperature of 95 °C. Indeed, we now could establish fairly uniform Fe doping concentrations during the growth of several hours.

3.2 Optimization of showerhead

After a few experiments, we observed black depositions solely at the first two of six small outlet holes in the showerhead which is responsible for distributing the $FeCl_2$ evenly over the growth region. This indicates that most of the dopant is leaving the showerhead at the upstream end of the growth zone. Due to the reactor geometry, the general flow of the carrier and source gases inside the growth zone is pointing backwards. Moreover, other tests indicated a leakage between the supply tube and the showerhead as a consequence of a gas blocking in the showerhead. This means that in this configuration a significant part of the $FeCl_2$ flow is transported away from the wafer, before it can contribute to any doping of the layer.

Therefore, a new showerhead was constructed which only contains one larger elliptical outlet hole directly over the growth zone instead of a few small ones.

By applying all construction details discussed above, two Fe-doped GaN layers with a thickness of about 1 mm have been deposited on templates grown by metalorganic vapor phase epitaxy. Facilitated by a hexagonal SiN mask, they spontaneously separated from the sapphire substrate by the thermal expansion mismatch between GaN and sapphire [2]. On the sample depicted in Fig. 1, a uniform Fe concentration of $2 \cdot 10^{18}\,\mathrm{cm}^{-3}$ has been determined by SIMS (Fig. 3) at several positions. However, the crystalline quality of this sample was not good enough for Hall experiments due to many internal cracks etc. Therefore, we used an optimized hexagonal SiO_2 mask for strain management for the second sample shown in Fig. 2. Although the self-separation did not work properly in the center of this sample, we could perform Hall experiments over a wide temperature range from room temperature up to 1000 K on the other areas confirming a semi-insulating behavior with a specific resistivity of about $10^7\,\Omega\mathrm{cm}$ at room temperature.

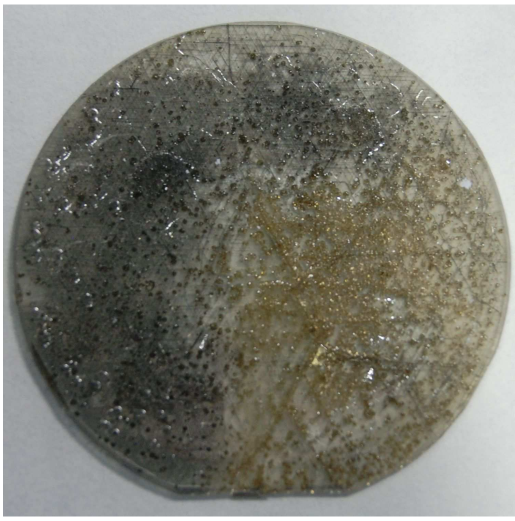

Fig. 1: Free-standing Fe-doped GaN sample on a template with 30 µm mask period. Fe content according to SIMS: $2 \cdot 10^{18}\,\mathrm{cm}^{-3}$.

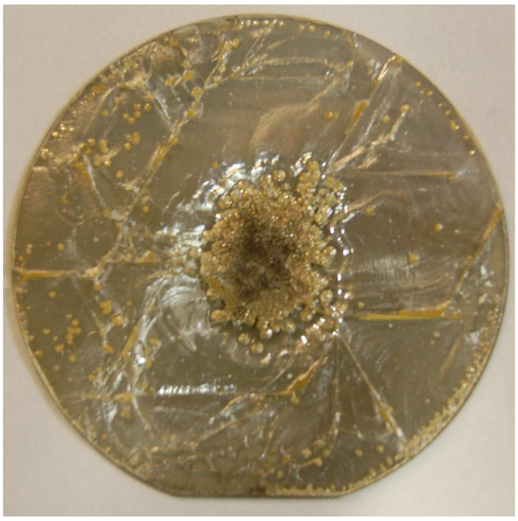

Fig. 2: Partly separated layer grown on a template with 15 µm mask period. According to van der Pauw Hall experiments: specific resistivity $\rho = 10^7\,\Omega\mathrm{cm}$.

4. Conclusion

In order to establish a controllable iron doping source for the growth of Fe-doped GaN, we have improved the metalorganic gas channel connected to our HVPE reactor. Owing to the low vapor pressure of ferrocene, a high bubbler temperature is required. Therefore,

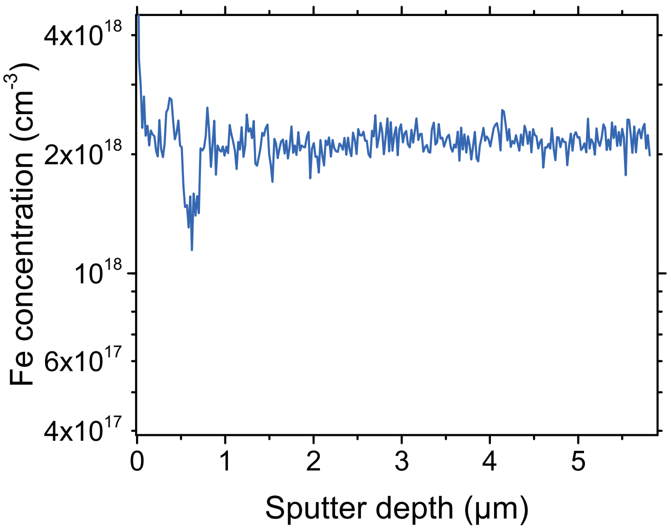

Fig. 3: SIMS profile of a free-standing GaN sample grown with ferrocene carrier gas pre-heating, measured down from the sample surface.

a pre-heating of the carrier gas was implemented, which stabilized the Fe supply over the full duration of an epitaxial run. Moreover, precursor gas losses in the reactor by unwanted backpressure could be minimized by changing the outlet hole design of the Fe showerhead. Now, uniformly doped thick GaN layers could be grown demonstrating semi-insulating behavior in temperature dependent Hall experiments.

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