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Concentrated chloride-based epitaxial growth of 4H-SiC

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Abstract. A chloride-based CVD process has been studied in concentrated growth conditions. A systematic study of different carrier flows and pressures has been done in order to get good quality epilayers on 8° off and on-axis substrates while using very low carrier flows. Hydrogen chloride (HCl) was added to the standard gas mixture to keep a high growth rate and to get homo-polytypic growth on on-axis substrates. The carrier flow was reduced down to one order of magnitude less than under typical growth condition. By lowering the process pressure it was possible to reduce precursor depletion along the susceptor which improved the thickness uniformity to below 2% variation (σ/mean) over a 2" diameter wafer.

Introduction

Chloride-based epitaxial growth [1] and low pressure/high temperature processes [2, 3] are commonly used in epitaxial growth of 4H-SiC to achieve high growth rates. Common to all these processes is the high flow of hydrogen as carrier gas. Today small scale research reactors for substrates with a few square centimeters large area, usually run with comparatively small carrier gas flows [4, 5]. The Si/H₂ ratios in these reactors are significantly higher than those commonly used in large CVD reactors. The high flow of hydrogen adds substantial cost and complexity to the process and the tools, making it desirable to develop a low carrier flow process capable of handling 2 – 3" diameter wafers where normally carrier flows between 50 – 150 slm would have been used.

In a previous study by Nakamura et al. [6] it was found that the growth rate is directly proportional to the partial pressure of the silicon precursor, to the square root of the carrier gas flow, and to the reciprocal of the process pressure. However, a systematic study on the effect of the pressure and carrier gas flow on high growth rate processes has not yet been done. Here we will present such a study using a chloride-based CVD process in a horizontal hot-wall reactor [7]. Small gas flows will require a low pressure to keep a proper gas speed in the reactor, but the process pressure cannot be lowered too much because a too low pressure would enhance etching [8,9]. Further, the use of high gas speed needs to be compensated by an efficient heating at the gas inlet to ensure a proper cracking of the precursors [2]. Low-pressure etching consists mainly in faster silicon evaporation from the surface, while lower hydrogen flows result in a reduced etching of carbon species [8]. The overall effect is a carbon rich atmosphere on the growing surface, which should be compensated by a silicon-rich gas supply. Another advantage of this low pressure process would be the reduced probability of silicon clusters formation in the gas phase at high silane flows, which degrades the epilayer morphology and is usually avoided by the addition of a chlorinated compound or use of a chlorinated precursor [10-12].

Experimental procedure

Two-inch diameter 4H-SiC wafers with an off-orientation of 8° towards the [11 $\bar{2}$ 0] direction and silicon-face on-axis 2x2 cm² samples were used as substrates. Rotation of the substrate was not done to be able to study the deposition rate along the susceptor. The reactor was initially evacuated and pumped to high vacuum, then filled with the carrier gas and brought to temperature and pressure setpoint before starting the growth. The cool down was done at 400 mbar. The precursors were silane (SiH₄), ethylene (C₂H₄), and hydrogen chloride (HCl), together with hydrogen as carrier

gas. The deposition time was usually 30 minutes giving epitaxial layer thicknesses in the 10 – 50 μm range depending on the growth conditions. The main experimental parameters were: Hydrogen flow (5 – 50 slm); Process pressure (10 – 200 mbar); Temperature (1500 – 1630 $^{\circ}\text{C}$); C/Si ratio (0.5 to 1.5); Cl/Si ratio (0 – 3); Ramp up conditions (with ethylene, or silane, or simply hydrogen at different flow and process pressure); Reaction chamber heating by using a different position of the reaction chamber with respect of the fixed RF coil.

The morphology of the layers was analyzed by Nomarski differential interference (NDIC) contrast optical microscopy and in greater detail using atomic force microscopy (AFM). The epilayers thickness was measured by Fourier transform infrared reflectance (FTIR). The material quality was analyzed by low-temperature photoluminescence (LTPL) at 2 K using the 244 nm line from an Argon excitation laser. The background doping concentration was measured either by capacitance-voltage (CV) measurement using a mercury-probe, or by LTPL [13].

Results and discussion

The growth conditions used in the standard chloride-based process [1] ($T = 1560\text{ }^{\circ}\text{C}$, $\text{H}_2 = 50\text{ slm}$, $P = 200\text{ mbar}$, $\text{Si}/\text{H}_2 = 0.66\%$, $\text{C}/\text{Si} = 1$, $\text{Cl}/\text{Si} = 3$) generated a growth rate of $80\text{ }\mu\text{m}/\text{h}$ on a $20\times 20\text{ mm}^2$ sample located at the gas inlet side of the susceptor. However on a 2" diameter 8° off-axis 4H-SiC wafer the calculated growth rate varied from 80 (gas inlet side) to $30\text{ }\mu\text{m}/\text{h}$ (gas outlet side), which means an average value of $55\text{ }\mu\text{m}/\text{h}$ with a very high non-uniformity.

In this study we completed a matrix of experiments changing the gas carrier flow (50 to 5 slm) and the process pressure (200 to 10 mbar) while keeping most of the remaining parameters constant. All the experimental results were in good agreement with the stagnant-layer model proposed by Nakamura et al. [6]. A reduction in hydrogen flow from 50 to 5 slm corresponded to a proportional decrease of growth rate especially in the outlet side of the susceptor; this trend was confirmed at different process pressures. Inversely, a decrease in pressure from 200 to 10 mbar favored an increase in growth rate up until the optimum gas speed was set in the system, after which the growth rate dropped.

The gas speed in the reactor is proportional to the total flow (comparable to the carrier flow) and to the reciprocal of process pressure [14]. By changing both carrier flow and pressure the gas speed was changed from 5 m/s to 110 m/s. As can be seen in Fig.1, the growth rate was higher at the gas inlet side of the susceptor at the lowest gas speed but the opposite holds true for the highest gas speed. At intermediate values of 37 m/s ($\text{H}_2 = 5\text{ slm}$, $P = 15\text{ mbar}$) the growth rate was averaged on the whole 2" substrate to a value of $55\text{ }\mu\text{m}/\text{h}$.

When using a high gas speed it is important to heat efficiently the precursors at the reaction chamber inlet [2] in order to crack them properly. This was done by increasing the growth temperature from the typical $1560\text{ }^{\circ}\text{C}$ to $1630\text{ }^{\circ}\text{C}$, and additional power was induced to the inlet section of the susceptor in order to increase the temperature of the incoming gas mixture. This led to an improvement of the morphology avoiding polycrystalline or triangular defects at the inlet part of the substrate, and also to a 20 % increase of growth rate.

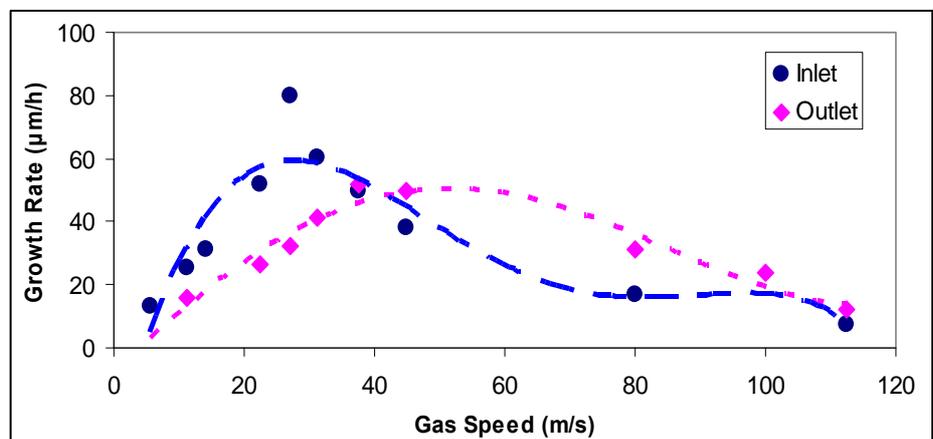


Fig. 1: Growth rate dependence on the gas speed on different parts of the susceptor (inlet and outlet) as measured on a 2" 8° off-axis 4H-SiC wafer. The curves are guides for the eyes.

As an added bonus in this optimization comes the opportunity in lowering of the Cl/Si ratio, which at the lower pressures (below 50 mbar) could be decreased to values lower than 1 thus reducing etching effects on the surface. This was possible due to the fact that at reduced pressures silicon clusters formation can be suppressed [15].

As discussed in the introduction section, due to the low pressure silicon evaporation is enhanced, while a reduced hydrogen flow minimizes carbon etching [8]. A silicon-rich supply is needed not only during growth but also during ramp up. The ramp up conditions were modified as well as compared to the process run at high carrier flow and high pressure. Therefore a smoother surface could be obtained by adding SiH₄ during ramp up, the amount to be used depended on the substrate off-angle: a small amount of 20 sccm for 8° off-axis substrates, 100 sccm for on-axis substrates with a subsequent 10 minutes etching at the growth temperature [16,17].

The C/Si ratio was slightly reduced as compared to standard growth conditions. For 8° off-axis substrates smoother and triangular defect-free surfaces were obtained at a C/Si ratio of 0.8, while for on-axis substrates a much lower C/Si of 0.5 was needed to get a homo-polytypic layer (Fig.2), together with a higher Cl/Si ratio of 3 as is usually needed for these substrates [18].

The morphology of the 8° off-axis epilayers grown at 55 μm/h is very good, as confirmed by NDIC microscopy (Fig. 3a), and AFM on a 10x10 μm² area with a RMS of 1.08 nm (Fig. 3b). LTPL confirmed the very good crystalline quality of the material, and it also provided the donor concentration measurement which was in the 10¹⁴cm⁻³ range, as confirmed also by CV measurements.

LTPL measurements on the on-axis samples confirmed the epitaxial layer to be 100% 4H-SiC of very high crystalline quality.

Conclusion

We have demonstrated an epitaxial process with a greatly reduced gas carrier flow of 5 slm (concentrated precursors condition), and much lower pressure (15 mbar) achieving a growth rate of 55 μm/h and a thickness non-uniformity below 2% (σ/mean) over a 2" 4H-SiC wafer, *without substrate rotation*. The advantages of these process conditions is the good thickness uniformity on a 2" wafer compared with the standard process but also the reduced process cost and reactor complexity and cost. This shows that it is possible to save big amounts of hydrogen and chlorinated

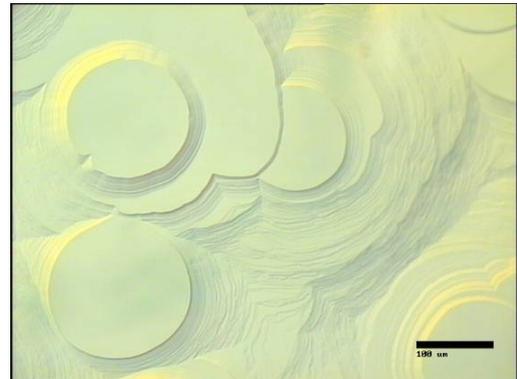


Fig. 2. NDIC image of an on-axis sample grown in Si-rich conditions at a growth rate of 35 μm/h. Magnification is 200X, the scale bar is 100 μm long.

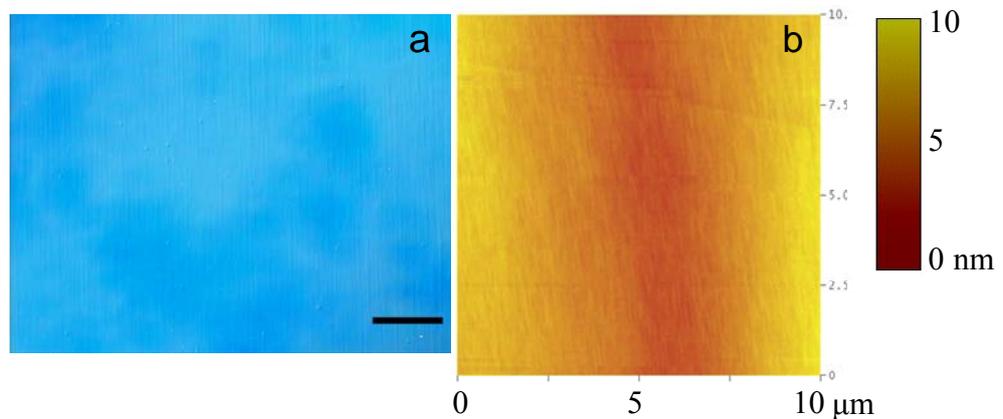


Fig. 3. Morphology of an 8° off-axis sample grown with a carrier flow of 5 slm and pressure of 15 mbar, with a growth rate of 55 μm/h, observed by: a) NDIC microscope with a magnification of 200X. The scale bar is 200 μm long; b) AFM on a 10x10 μm² area. The RMS value is 1.08 nm.

precursor at the cost of a small reduction in growth rate though with large improvements in uniformity.

Si-rich conditions were needed due to the reduced process pressure, therefore SiH₄ ramp-up and C/Si ratios lower than usual were adopted both for 8 °off-axis and on-axis substrates. Cl/Si ratios lower than usual were used thanks to reduced Si-clusters formation, higher temperature and additional power at the susceptor inlet were needed for a proper cracking of the precursors flowing at high speed.

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