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Reduction of structural defects in thick 4H-SiC epitaxial layers grown on 4° off-axis substrates

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By carefully controlling the surface chemistry of the chemical vapor deposition process for silicon carbide (SiC), 100 μm thick epitaxial layers with excellent morphology were grown on 4° off-axis SiC substrates at growth rates exceeding 100 $\mu\text{m}/\text{h}$. In order to reduce the formation of step bunching and structural defects, mainly triangular defects, the effect of varying parameters such as growth temperature, C/Si ratio, Cl/Si ratio, Si/H₂ ratio, and *in situ* pre-growth surface etching time are studied. It was found that an *in-situ* pre growth etch at growth temperature and pressure using 0.6% HCl in hydrogen for 12 min reduced the structural defects by etching preferentially on surface damages of the substrate surface. By then applying a slightly lower growth temperature of 1575 °C, a C/Si ratio of 0.8, and a Cl/Si ratio of 5, 100 μm thick, step-bunch free epitaxial layer with a minimum triangular defect density and excellent morphology could be grown, thus enabling SiC power device structures to be grown on 4° off axis SiC substrates. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4809928>]

I. INTRODUCTION

Silicon carbide (SiC) is a promising material for high power and high frequency devices due to its high breakdown electric field, high thermal conductivity, and high saturation electron drift velocity.^{1,2} In order to realize very high voltage (>10 kV) SiC devices, thick (>100 μm), low doped (<10¹⁵ cm⁻³) epitaxial layers with good morphology are needed.³ For homoepitaxial growth of SiC, substrates are usually cut not orthogonally to the c-axis but a few degrees off rendering a surface with atomic steps to facilitate step-flow controlled epitaxial growth.⁴ Growth of epitaxial layers on 4H-SiC substrate with an off-cut of 8° towards the [11–20] direction yields less surface defects. However, a large off-angle reduces the number of wafers that can be sliced from a single crystal boule, leading to a substantial amount of wasted material, especially for 4 in. and 6 in. wafers. The use of lower off-cut angle decreases the material loss, thereby reducing the total cost for the final device. It has also been reported that the use of 4° off-angle substrates leads to reduction of basal plane dislocations (BPD) in the epitaxial layers compared to the 8° off-angle substrates.^{5,6} The presence and propagation of the BPD in the epitaxial layers are known to cause a drift of the forward voltage in bipolar devices during operation.^{7,8} The use of a high growth rate or low C/Si during the epitaxial growth increases the density of BPD in the epitaxial layers, according to the studies made by Ohno *et al.*⁹ Also the density of BPD in the epitaxial layers has been reduced using *in situ* growth interrupts¹⁰ or molten potassium hydroxide (KOH) etching.¹¹ However, the main disadvantages of using 4° off-angle substrate are usually the formation of step bunching^{12,13} or triangular defects of different shapes and widths¹⁴ on the epitaxial layers. The step bunching negatively influences the

device performance,¹⁵ and it has been proposed that the use of a low C/Si ratio during growth⁵ as well as epitaxial growth on the C-face of the substrate¹⁴ reduces the step bunching. Furthermore, it has been reported that the density of the triangular defects could be reduced using a low C/Si ratio¹⁶ or a higher Cl/Si ratio¹⁷ during the growth. The formation of step bunching and structural defects on the surface can be avoided by carefully controlling the surface chemistry in the growth process. In this paper, we systematically study the effects on the surface chemistry by systematically varying the growth temperature and the chemical vapor deposition (CVD) gas mixture by changing C/Si-ratio, Cl/Si-ratio, and Si/H₂ ratio. Also the effect of *in situ* etching time prior to growth was studied. The optimal surface chemistry was used to demonstrate growth of >100 μm thick epitaxial layers of 4H-SiC on 4° off-axis (0001) Si-face substrates at growth rates >100 $\mu\text{m}/\text{h}$ with good morphology.

II. EXPERIMENTS

Growth experiments were performed in a horizontal flow hot wall chemical vapor deposition reactor without rotation of the substrate. All substrates in this study were approximately 1.5 × 1.5 cm² samples cut from one chemomechanically polished 4 in. 4H-SiC wafer with a 4° off-cut towards the [11–20] direction; growth was done on the Si-face of the substrates. For all experiments, the growth pressure and growth time were kept constant at 100 mbar and 1 h, respectively. Palladium membrane purified H₂ was used as carrier gas. The carrier gas flow was 50 l/min, SiH₄ (silane) + C₂H₄ (ethylene) + HCl were used as precursor with a Si/H₂ ratio of 0.25%. The growth temperature was varied in the 1550–1625 °C range, the C/Si ratio was varied between 0.4 and 1.1 by changing the C₂H₄ flow, the Cl/Si ratio was varied between 5 and 8 by changing the HCl flow. For surface preparation, a HCl flow of 300 ml/min was added to the H₂ flow when the temperature in the growth chamber

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was 1175 °C, the HCl flow was kept constant during the temperature ramp up to the growth temperature and followed by etching at growth temperature for between 0 and 24 min, after which the precursors were gradually introduced to the gas mixture. The precursor flows are ramped up from low flows to the growth process flows during 3 min, maintaining the C/Si and Cl/Si ratios. No intentional dopants were added in this study. The thicknesses of the layers were measured by observing the cross section of cleaved samples in an optical microscope. The morphology of the epitaxial layers was studied by an optical microscope with Nomarski differential interference contrast (NDIC) and in greater detail with atomic force microscopy (AFM) in tapping mode. AFM measurements were done on a $20 \times 20 \mu\text{m}^2$ surface at the center of the substrate and at two different areas at the periphery, about 2 mm from the edge. The surface roughness of the samples was quantified by the root mean square (RMS) value of the height variations over the area scanned by AFM. The net carrier concentration of the epitaxial layers was determined from capacitance-voltage (CV) measurements using a mercury-probe. Low temperature photoluminescence (LTPL) at 2 K with a frequency doubled Argon ion laser at 244 nm was used to estimate the quality of the grown epitaxial layers. In addition, the LTPL spectra of all samples were processed according to the procedure of (Ref. 18) in order to obtain the nitrogen-doping concentration, which is in excellent agreement with the net carrier concentration obtained for those samples where CV measurements were possible. Raman measurements were performed in a micro-Raman setup with spatial resolution (size of the laser spot) $< 1 \mu\text{m}$ using a 532 nm laser as an excitation source. In order to estimate and compare dislocation densities in epitaxial layers grown under different growth conditions, the epitaxial layers and substrates were etched in molten KOH at 500 °C for 3 min to decorate dislocations on the epitaxial layer surface. The shape and distribution of etch pits were studied by optical microscopy. The investigated areas excluded 2 mm from the edge.

III. RESULTS AND DISCUSSION

The surface chemistry of the CVD process was studied by isolating the effect of temperature, C/Si ratio, etching time, Cl/Si ratio, and Si/H₂ ratio by varying etch parameter while keeping the other fixed. The effect on the morphology and surface roughness was determined by NDIC microscopy

and AFM, respectively. The dislocation densities in the substrates were found to be 4×10^3 – 5×10^3 , 2×10^3 – 3×10^3 , and 9×10^2 – $1 \times 10^3 \text{ cm}^{-2}$ for BPD, threading edge dislocations (TED), and threading screw dislocations (TSD), respectively. Most BPD in the substrate were converted to TED in the grown epitaxial layers, for all growth conditions. It can be seen by the significantly lower BPD density and higher TED density in the epitaxial layers compared to the substrate; this is consistent with previous results.⁹

A. Growth temperature

The effect of growth temperature was studied in the 1550–1625 °C range with C/Si fixed at 0.9, etching time at 12 min and Cl/Si at 5 (Fig. 1). Triangular defects were observed in all epitaxial layers. At the lowest growth temperature (1550 °C), a high density, 12 cm^{-2} , of the triangular defects was observed. Besides those defects, the observed surfaces are smooth having a RMS surface roughness of about 1.3 nm on a $20 \times 20 \mu\text{m}^2$ area. At the highest temperature (1625 °C) severe step bunching with 150–950 nm wide terraces and 5–6 nm step height were formed. The density of triangular defects decreased somewhat at this temperature to 7 cm^{-2} . It has been reported that the different step velocities for each Si-C bilayer, due to the difference in energy cost deposition (the extra energy for adding a new layer), promote the formation of half-unit-cell height step. Periodically, changing bond configuration at step edges with the half-unit-cell height may further induce bunching of these steps into unit-cell height (1 nm) steps.¹² The more severe step bunching at higher growth temperature is most likely explained by enhanced surface migration at higher growth temperature, allowing species to migrate faster on the SiC surface where the difference in growth rate at steps and at the terraces is increased resulting in increased step bunching. The growth temperature was not found to affect the dislocation densities in the grown epitaxial layers, which were found to be 400–500, 6×10^3 – 8×10^3 , and 9×10^2 – $1 \times 10^3 \text{ cm}^{-2}$ for BPD, TED, and TSD, respectively.

Based on these results, in order to reduce the formation of step bunching and triangular defects a growth temperature of 1575 °C was chosen for the following experiments.

B. C/Si ratio

The effect of the C/Si ratio on the surface chemistry was studied in a set of experiments with a fixed Cl/Si of 5,

FIG. 1. Optical microscope images at 200 times magnification of 115 μm thick 4H-SiC epitaxial layers with C/Si = 0.9, Cl/Si = 5, Si/H₂ = 0.25%, and growth rate = 112 $\mu\text{m/h}$ for various GT.

FIG. 2. Optical microscope images at 200 times magnification of 4H-SiC epitaxial layers grown at temperature = 1575 °C, Cl/Si = 5, growth time = 1 h, Si/H₂ = 0.25%, and various C/Si ratios.

etching time at growth temperature of 12 min, with the C/Si ratio varied between 0.4 and 1.1 at growth temperatures of 1575 °C (Fig. 2).

The best morphology was obtained at C/Si ratio of 0.8 having a RMS value of 0.95 nm and the triangular defects density of 8 cm⁻². At C/Si ratios above 0.8, the surface morphology deteriorated, as manifested by higher RMS values and at C/Si ratios below 0.8, severe step bunching and RMS values up to 32 nm was observed (Fig. 3(a)). The growth rate for various C/Si ratios is plotted in Fig. 3(b), which illustrates that the growth rate drops when the C/Si is below 0.9, since the growth becomes carbon limited and the growth rate thus decreases due to the lack of carbon.^{19,20} The density of the triangular defects decreased with decreasing C/Si ratio from 1.1 to 0.4 (Fig. 3(c)). Similar tendency has been reported earlier¹⁶ and was attributed to decrease of growth rate at lower C/Si.

Fig. 4 displays the AFM images of the epitaxial layers grown at C/Si < 0.8. For C/Si ratios of 0.7 and 0.6, severe step bunching with 58–102 nm and 25–82 nm high steps, respectively, was observed. The terrace width was irregularly distributed ranging between 1–2 μm and 0.5–1.2 μm for C/Si ratios of 0.7 and 0.6, respectively. The step height decreased to 15–17 nm and 11–13 nm and terrace width to 430–460 nm and 280–450 nm for C/Si ratios of 0.5 and 0.4, respectively. It has previously been reported that the step separation depends on the C/Si ratio.^{5,14} The formation of the step bunching has been explained by a model based on the impurity effect.^{21,22} Ishida *et al.* reported the formation of extreme step bunching at very low or high C/Si ratio.²³ They suggested that the severe step bunching is formed by the appearance of Si clusters or C clusters on the terraces due to excessive flow of SiH₄ or C₃H₈. At C/Si ratios of 0.7 and 0.6, epitaxial layers with a very rough surface, having a RMS value of 32 and 28 nm, respectively, (Fig. 3(a)), and severe step bunching due to excessive flow of SiH₄ were observed. On the other hand, at lower C/Si ratio, 0.5 and 0.4 the step height and terrace width of the step bunching decreased. At lower C/Si ratio the growth rate is much lower (36 μm/h for C/Si of 0.4 and 95 μm/h for C/Si of 0.7) which results in a reduced step bunching. Experiments have been performed at C/Si of 0.7, Si/H₂ of 0.125% and growth time of 60 and 120 min to investigate the effect of growth rate on the step bunching while severe step bunching was observed at Si/H₂ of 0.25% as mentioned above. Step height and terrace width decreased to 13–15 nm and 410–440 nm,

FIG. 3. Dependencies of (a) RMS value; (b) growth rate; (c) triangular defects density on the C/Si ratio for 4H-SiC epitaxial layers with growth temperature = 1575 °C, Cl/Si = 5, and Si/H₂ = 0.25%.

FIG. 4. AFM images of a $4 \times 4 \mu\text{m}^2$ area of epitaxial layers with growth temperature = 1575°C , $\text{Cl/Si} = 5$, growth time = 63 min and $\text{Si/H}_2 = 0.25\%$, and various C/Si ratios.

respectively, when the growth rate was decreased to about $45 \mu\text{m/h}$. The growth time (i.e., growing thicker epitaxial layers with the same growth rate) had no influence on the step bunching. The BPD and TED densities were not affected by the C/Si ratio, while the TSD density was found to increase significantly at $\text{C/Si} < 0.8$. This can be explained by the increased probability for conversion of micropipes into TSD at low C/Si ratio.²⁴

C. *In-situ* surface preparation

It has previously been shown that proper surface preparation prior to the epitaxial growth will reduce the amount of surface defects on the substrates, which is the key for growing epitaxial layers of good quality.²⁵ In our previous study, we investigated the effect of different conditions during the temperature ramp-up prior to epitaxial growth on the carrot defect formation during epitaxial growth on 8° off axis substrates.²⁶ Also a HCl *in situ* etching prior to epitaxial growth at a temperature 50°C higher than the growth temperature for the growth of about $20 \mu\text{m}$ thick 4H-SiC epitaxial layers grown on 4° off axis substrates has been used.²⁷ As mentioned above, the best morphology was obtained at C/Si ratio of 0.8 and 1575°C . At this temperature, where the etching time at growth temperature was 12 min, the density of triangular defects was still high (8 cm^{-2}). In order to reduce the density of the triangular defects, a set of growth experiments was done with fixed C/Si of 0.8, Cl/Si of 5 and growth temperature of 1575°C , while the etching time at growth temperature was varied between 0 and 24 min (Fig. 5). Epitaxial layers with the lowest triangular defects density (2 cm^{-2}) and roughness, having a RMS value of 0.75 nm , were obtained with an etching time of 18 min at the growth temperature. Etching times of 0, 6, and 24 min at the growth temperature results in layers with very high triangular

defects density and very bad morphology, as illustrated in Fig. 5. The chemistry of the SiC surface etching can be explained as follows: hydrogen molecules or atoms react with surface C atoms forming hydrocarbons, allowing carbon to be removed from the surface. With the high flow of H_2 at the low pressure, C will be efficiently removed from the SiC lattice.²⁸ Similar reactions between hydrogen and silicon atoms are slower leading to a faster removal of carbon than silicon from the surface, when etching is done in pure hydrogen ambient. Addition of HCl will increase the desorption of silicon from the surface through reactions between Si and Cl and possibly also H atoms forming of SiH_xCl_y species. Etching of carbon by chlorine is not likely given the lower bond enthalpy for C-Cl 324 kJ mol^{-1} compared to C-H 414 kJ mol^{-1} .²⁹ For comparison the bond enthalpies for Si-Cl and Si-H are 400, respectively, 323 kJ mol^{-1} (Ref. 29), indicating that Si will mainly be etched by Cl. Thus the addition of HCl will lead to an etch process that removes Si and C at similar rates which enables a smoother SiC surface with less surface defects.³⁰ An etching time between 0 and 6 min was found to be too short to achieve a smooth surface, whereas for an etching time of 24 min the etching is too long, resulting in a severely damaged surface. We observed a similar trend in the reduction of the carrot defect density in our previous study.²⁶ It seems that the mechanisms for the formation of triangular and carrot defects are quite similar, and the concentration of defects can be controlled by an *in-situ* surface etch.

The best *in situ* etching condition of 18 min had a great impact also on the BPD density, which was reduced from 250 cm^{-2} for an etching time of 12 min to below 10 cm^{-2} . It has previously been reported¹¹ that the creation of BPD etch pits on the substrate surface after molten KOH etching enhanced the conversion of BPD into TED during epitaxial layers growth. This effect also increases as the dimension of

FIG. 5. Optical microscope images at 200 times magnification of 4H-SiC epitaxial layers with growth temperature = 1575°C , C/Si = 0.8, Cl/Si = 5, growth rate = $105 \mu\text{m/h}$, and $\text{Si/H}_2 = 0.25\%$ for various etching time at growth temperature.

the BPD etch pits on the substrates became larger. It can thus be speculated that as the etching time at growth temperature increased, the BPD etch pits on the substrates became larger which facilitated the conversion of BPD into TED. The etching times of 0, 6, and 24 min at growth temperature results in layers with very high triangular defects density and very bad morphology, which makes it impossible to count the etch pits of the dislocations. The densities of TED and TSD was not affected by the etching time and remained in the high and low 10^3 cm^{-2} ranges, respectively.

D. Cl/Si ratio

The impact of the Cl/Si ratio was probed by experiments with fixed C/Si ratio of 0.8 and a 18 min etching time at growth temperature and a varying Cl/Si ratio between 5 and 8. The density of triangular defects for various Cl/Si ratios were in the order of $2 \pm \text{cm}^{-2}$. The epitaxial layers with the lowest defects density (1.2 cm^{-2}) but a rougher surface with a RMS value of 1.56 nm was obtained at a Cl/Si ratio of 7.5. The smoothest surface having a RMS value of 0.75 nm was observed at Cl/Si of 5, 5.5, and 6, but the triangular defects density was then 2 cm^{-2} . The growth rate was constant for Cl/Si ratios below 6 and decreased for Cl/Si > 6 (Fig. 6). The effect of Cl/Si ratio on the morphology of the epitaxial layers³¹ and on the growth rate^{32,33} has been reported previously. A decrease in growth rate for lower Cl/Si ratio³³ due to insufficient formation of SiCl_2 and for higher Cl/Si ratio³² due to etching of the growing epitaxial layers was found. At Cl/Si ratio of 5, 5.5, and 6, the growth rate is more or less constant, while for Cl/Si > 6 , the etching rate of the growing epitaxial layer becomes so significant that the result is a decreased growth rate. The Cl/Si ratio was not found to affect the dislocation densities.

E. Growth rate

To investigate the impact of the growth rate on the surface roughness and triangular defects density, experiments at different growth rates with C/Si at 0.8, 18 min etching time at growth temperature, growth time of 1 h, and Cl/Si of 6 were performed. The growth rate was controlled by varying

FIG. 6. Dependence of the growth rate on the Cl/Si ratio for 4H-SiC epitaxial layers with growth temperature = 1575 °C, C/Si = 0.8, etching time at growth temperature = 18 min, and $\text{Si}/\text{H}_2 = 0.25\%$.

the Si/H_2 ratio between 0.15% and 0.25% rendering growth rates between 65 and 105 $\mu\text{m}/\text{h}$ (Fig. 7). The triangular defects density and RMS value were not affected by the growth rate in the investigated range, remaining at $\sim 2 \text{ cm}^{-2}$ and 0.75 nm, respectively. The growth rate was not found to affect the dislocation densities. This is contradictory to the paper by Ohno *et al.*,⁹ where it was reported that the BPD density was increased with increasing growth rate. It should be mentioned that all epitaxial layers in their study were grown on 8° off axis substrates and the growth rate was in the range of 4–10 $\mu\text{m}/\text{h}$, while in our study, epitaxial layers were grown on 4° off axis substrates and the growth rate was in the range of 65–105 $\mu\text{m}/\text{h}$.

F. Characterization of the triangular defects

The triangular defects were observed in all samples; however, their structure was different depending on the C/Si ratio, as illustrated in Fig. 8. It can be seen that, for C/Si ratios in the range 0.4–0.8, the inside of the triangular defect is completely covered by defects, whereas for larger C/Si (0.9–1.1) the inner part looks smoother, but a linear defect emerges in the middle of the triangle. It was found during our investigations that the triangular defect length is proportional to the epitaxial layer thickness and can be estimated by

$$\text{epitaxial layer thickness} = \tan(4^\circ) \times \text{triangular defect length}.$$

Here, the angle of 4° is the off-cut angle of the substrates. Similar calculation is applicable in case of the carrot defects observed on 8° off cut substrates.³⁴

In order to get insight in the structure of the triangular defects, LTPL and Raman measurements were carried out on the defect area within the triangles. The LTPL spectra showed none, or in some cases, strongly diminished luminescence of the usual near-band gap emission of the 4H-SiC polytype, with no detectable contribution from other polytypes. However, the micro-Raman spectrum, taken within the two types of triangles shown in Fig. 8, showed distinct difference from the spectrum taken outside the defect (on the smooth surface of the samples far from any triangular

FIG. 7. Dependence of the growth rate on the Si/H_2 ratio for the 4H-SiC epitaxial layers grown at 1575 °C, with C/Si = 0.8, etching time at growth temperature = 18 min, and Cl/Si = 6.

FIG. 8. Optical microscope images at 50 times magnification of triangular defects having different structure depending on the C/Si ratio.

defects). The outcome of the Raman measurements is summarized in Fig. 9. As expected, the spectra taken on the sample surface with no visible defects show the typical Raman spectrum of the 4H polytype in backscattering geometry from the (0001) face of the crystal³⁵ (Fig. 9(a)). On the other hand, the spectrum taken within a triangular defect are different in the ratio between the Raman peaks at 777 and 797 cm^{-1} , as well as in the appearance of the longitudinal optical (LO) mode, which is positioned at 966 cm^{-1} in a pure 4H-SiC sample in the above-mentioned geometry. More concretely, the spectrum within the triangular defects show an enlarged contribution of the 797 cm^{-1} mode compared to the 777 cm^{-1} one, and at the same time the LO peak splits into two distinct peaks at 965 and 972 cm^{-1} . Similar spectra have been observed previously³⁶ when 3C-SiC inclusions are imbedded in the 4H-SiC crystal. Indeed, the 3C-SiC polytype exhibits only two Raman peaks at 797 and 972 cm^{-1} . Hence, if there exists 3C inclusions within the probing laser spot (about 1 μm in diameter in our experiment), their Raman-spectrum will contribute to the spectrum

of the 4H polytype, which is present within the same spot. This will lead to changed ratio in the intensities of the 797 cm^{-1} (originating from both 3C- and 4H-SiC) and the 777 cm^{-1} peaks (4H only), and simultaneously show the 965 cm^{-1} mode of 4H-SiC together with the 972 cm^{-1} mode of 3C-SiC. This situation is depicted in Fig. 9(b). In addition, we have mapped (using micro-Raman spectroscopy) a line across the two types of triangles shown in Fig. 8. In both cases, the Raman spectra within the triangle show the contribution of the 3C polytype, as described above. However, in the case of the triangular defect typical for low C/Si ratios (Fig. 8(a)) the contribution of the 3C-spectrum to that of the 4H-polytype is quite random from point to point (the distance between the subsequent points is 10 μm), whereas this contribution increases smoothly when the laser spot is scanned across the triangle in the direction shown with arrow in Fig. 8(b). This is an evidence that triangles similar to the one in Fig. 8(a) (low C/Si ratio) are filled with microscopic randomly distributed inclusions of 3C-SiC. One might suspect that the triangle would be filled with stacking faults rather than inclusions of an second SiC phase, however, inclusions of 3C-SiC rather than stacking faults are the most probable explanation for the appearance of the peak at 972 cm^{-1} and the increase of the 797 cm^{-1} peak, the contribution of those peaks in the 4H-SiC Raman spectrum is too high to be attributed to stacking faults. Further, stacking faults would represent too small fraction in the volume probed by the laser spot, too small to account for the observed intensity in the above mentioned peaks. The smooth decrease of the contribution of the 3C polytype in the Raman spectra taken across a triangle similar to the one in Fig. 8(b) (high C/Si ratio), together with the rather smooth morphology within the defect, suggests that a plausible explanation in this case would be a single crystal of 3C-SiC within the triangle, the thickness of which increases along the arrow in Fig. 8(b). In all cases, the spectra anywhere outside the triangles are identical to the one in Fig. 9(a), indicating sole contribution from the (0001) surface of 4H-SiC. We note also that polytype inclusions other than 3C-SiC would likely produce minor peaks associated with the zone folding.³⁷ Such minor peaks are the peaks at the 266 cm^{-1} and 610 cm^{-1} , and the doublet 196–204 cm^{-1} , which uniquely identify the contribution of the 4H polytype.³⁵ This leads us to conclude that the observed intensity variations discussed above are entirely due to the interplay of the contributions

FIG. 9. (Raman) (a) Raman spectrum of 4H-SiC in backscattering geometry from the (0001) surface, representative for all samples on a defect-free surface, and (b) typical spectrum when the laser spot is within a triangular defect of the type shown in Fig. 8(b). The latter spectrum shows contribution from both 4H and 3C polytypes and is similar to the spectra obtained also from the other type of triangular defects shown in Fig. 8(a). The spectra are recorded at room temperature using an excitation a 532 nm laser line. The peaks are labeled with their respective Raman shift in cm^{-1} .

FIG. 10. (PL) LTPL spectra of (a) sample with one of the lowest background doping levels, $[N] = 1.3 \times 10^{12} \text{ cm}^{-3}$, and (b) sample with high background doping, $[N] = 1 \times 10^{15} \text{ cm}^{-3}$. P_0 and Q_0 denote the no-phonon lines of the N-bound exciton. Some of the prominent phonon replicas of the N-bound P_0 line (respectively, the free exciton) are denoted with the letter P (respectively, I) and a subscript showing the approximate energy of the involved phonon, in a common notation. Note that spectrum (a) is entirely dominated by the emission from the free-exciton recombination, yet the Q_0 line is observable and used to determine the nitrogen background doping. The insert shows the PL emission in the whole spectral region measured, illustrating the contribution from the DI center, as well as no detectable contribution from other defects or polytypes.

of 3C and 4H-SiC in the spectra and no other polytypes are involved.

G. Background doping concentration

The unintentional nitrogen doping in all samples was estimated using the LTPL spectra according to the procedure described in Ref. 18. For samples with higher doping level ($>10^{14} \text{ cm}^{-3}$) CV measurements of the net doping concentration were also possible and in all cases the net doping concentration (donor concentration minus acceptor concentration) determined by CV coincides within $<5\%$ with the nitrogen doping concentration determined by LTPL. This suggests that the acceptor concentration in our samples is negligible and the detected donor concentration is entirely due to unintentional doping with nitrogen. LTPL spectra of the samples with the lowest and highest doping levels are

shown in Fig. 10. The spectra are dominated by the contribution of the nitrogen-donor-bound exciton (zero-phonon line and its phonon replicas) and the phonon replicas of the free exciton, with no detectable contribution from, e.g., the Al acceptor bound exciton, thus confirming that the unintentional doping is mainly due to the nitrogen donors. Apart from the near-bandgap emission comprising the lines associated with the nitrogen-bound exciton and the free exciton, the LTPL spectra show also some emission (see insert, Fig. 10) from the well-known but unidentified DI center;³⁷ however, in most samples its intensity is weak, similar to that in samples grown by usual (non-chlorine based) CVD epitaxy, hence its contribution to the net doping concentration is most likely negligible.

The nitrogen doping dependence on the C/Si ratio is displayed in Fig. 11(a), which illustrates that the lowest doping is achieved at the highest C/Si ratio of 1.1. This trend is consistent with the site-competition model,³⁸ and clearly observed for $C/Si > 0.7$. On the other hand, at $C/Si = 0.7$ the doping increases abruptly by almost two orders of magnitude, however decreases for lower C/Si ratios in contrast to our expectation with respect to the site competition. In order to explain this phenomenon, we recall that at $C/Si = 0.7$ also the most severe the step bunching was observed with largest step height, as mentioned in Sec. III B. This suggests that the large increase of doping might be connected to the increased height of the steps. Indeed, for decreasing C/Si below 0.7, the step height decreases (Fig. 3) and at the same time the doping decreases, as shown in Fig. 10, which suggests that the nitrogen incorporation is favored by higher steps on the surface of the growing film. This is consistent with the previous results^{39,40} where it was shown that nitrogen atoms are incorporated at steps in step-controlled epitaxy growth with a sticking coefficient of almost unity.

The impact of the growth rate on the doping is illustrated in Fig. 11(b). The doping increases as the growth rate decreases, as expected, since at lower growth rate the probability for incorporation of nitrogen atoms is larger resulting in higher doping. However, no visible impact of the Cl/Si ratio on the doping level was observed. Pedersen *et al.*⁴¹ reported that the doping level was increased with increasing Cl/Si-ratio. It should be mentioned that all epitaxial layers in that study were grown on 8° off axis substrates and intentionally doped using N_2 -gas and the Cl/Si ratios were 2 to 4, while in our study epitaxial layers were unintentionally doped and the Cl/Si ratios were 5 to 8.

FIG. 11. Background doping concentration of 4H-SiC epitaxial layers with growth temperature = 1575°C : (a) at various C/Si ratios, (b) at various Si/ H_2 and C/Si = 0.8.

IV. CONCLUSIONS

In this study, we have demonstrated growth of 100 μm thick, step-bunch free, i.e., with a step height lower than 0.25 nm, epitaxial layer with minimum triangular defects density and very good morphology on 4° off-axis Si-face substrate at growth rates exceeding 100 $\mu\text{m}/\text{h}$ by a process optimization of the chloride-based CVD.

- At the lowest growth temperature (1550 °C) a higher density of the triangular defects was observed, while at the highest one (1625 °C) severe step bunching appeared. An optimal growth temperature of 1575 °C produced step-bunch free epitaxial layer with less triangular defects.
- The triangular defects density decreased as C/Si decreased due to decrease of growth rate at lower C/Si. The best condition was obtained at C/Si of 0.8. At C/Si ratio above 0.8, the surface morphology deteriorated and at C/Si ratio below 0.8 severe step bunching was observed (Fig. 3).
- Epitaxial layers with the lowest triangular defects density and lowest surface roughness were obtained with etching time of 18 min at growth temperature.
- At Cl/Si = 7.5 the triangular defects density decreased but a rougher surface was obtained, an optimum Cl/Si value of 6 was found.
- The growth rate did not influence the triangular defects density and surface roughness.
- The density of TSD in the epitaxial layers was increased by a low C/Si ratio due to increased probability for conversion of micropipes into TSD at low C/Si ratio. The density of BPD in the epitaxial layers was reduced by proper *in situ* etching time, the density of TED in the epitaxial layers was not found to be affected to any larger extent by any change in growth conditions.
- Raman spectra taken from within the triangular defects show the contribution of the 3C polytype. It is further suggested that depending on the C/Si, the 3C-SiC within the triangular defects change from single crystal, at high C/Si, to polycrystalline at low C/Si.
- The epitaxial layers with good morphology all show a very intense near bandgap LTPL emission, indicating that the epitaxial layers are of high crystalline quality.

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