4H-SiC homoepitaxy on nearly on-axis substrates using TFS- towards high quality epitaxial growth

Anusha Balachandran^{1*}, Haizheng Song¹, T.S. Sudarshan¹, M.V.S. Chandrashekhar¹

¹Department of Electrical Engineering, University of South Carolina, Columbia, SC 29208, U.S.A.

* Corresponding author email address: balachaa@email.sc.edu

Abstract

We report high quality homoepitaxial growth on nearly on-axis ($\pm 0.5^\circ$) 4H-SiC substrates by chemical vapor deposition (CVD) using Tetrafluorosilane and Propane as Si and C-precursors, respectively. N-type unintentional doping (10^{17} cm^{-3} to 10^{14} cm^{-3}) was obtained for $0.6 < \text{C/Si} < 2.5$, displaying site-competition behavior. Epilayers showing varying degrees of step flow/spiral growth were obtained at growth rates R_g - 5-14 $\mu\text{m/hr}$, which was found to be C-controlled. At $\text{C/Si} < 2$, R_g was weakly dependent on the ratio, with a clear transition from step-controlled growth ($0.6 < \text{C/Si} < 1$) to spiral growth as C/Si increases, as observed by others previously. For $\text{C/Si} > 2.0$, a linear dependence on C-flow is established, with a return to step-mediated growth, shown by the surface morphology (RMS roughness $\sim 1 \text{ nm}$), and high polytype uniformity from Raman at high R_g - 14 $\mu\text{m/hr}$. These two behaviors were ascribed to a decrease in the etch rate of SiC by SiF_4 with increasing C/Si due to C-aided decomposition of SiF_4 , both of which make available a greater amount of elemental Si at the surface, thereby suppressing spiral growth. Use of on-axis or near on-axis substrates can eliminate/reduce basal plane dislocations which limit the performance of SiC bipolar electronic devices.

Keywords: A3.SiC epitaxy, A3.On-axis SiC growth, A1.Raman characterization, A3. Chemical vapor deposition process, B1.Tetrafluorosilane

Introduction

4H-SiC is a wide band gap semiconductor for producing high power ($>3\text{kV}$) and high temperature electronic devices[1], which require thick high quality epitaxial layers, $>30\mu\text{m}$. Homoepitaxial growth of 4H-SiC by Chemical Vapor Deposition (CVD) is the key enabling technology for improving the quality of these thick SiC films. These films often suffer from polytype inclusions, with SiC displaying >200 polytypes, with bandgaps varying from 2.3eV for the thermodynamically favorable 3C cubic polytype to 3.4eV for the 2H hexagonal polytype. The difference among the various SiC polytypes is the stacking sequence of double layers of Si and C atoms. The stacking sequence in the (0001) direction for the hexagonal polytype (also known as α -SiC) 4H is ABCB..., where A, B, and C represent the three possible positions of the double layers. The stacking sequence for the cubic 3C polytype, also known as β -SiC, in (111) direction is ABC. Change in the stacking sequence has a profound effect on the electrical properties [2].

The most important polytype for electronic devices is 4H-SiC (bandgap 3.2eV) [3]. However replicating polytype without extraneous polytypes (e.g. 3C) is critical to ensure high quality epitaxial layers for device fabrication. This replication is called homoepitaxy, and is typically done on off-axis substrates. The high surface density steps with off-axis substrates provides template sites for growth species to stick to the surface and replicate the substrate stacking structure. This mechanism is termed step-flow growth[4]. Epilayers with high polytype uniformity and specular surfaces are generally possible with off-oriented substrates.

However homoepitaxy on off-axis substrates has several disadvantages such as: slicing the wafer from an on-axis growth boule resulting in greater material losses $>50\%$ as substrate diameter increases especially for 8° offcut, 4" and 6" wafers, with corresponding increase in cost [5]. Growth on off-axis substrates results in a greater likelihood of propagation of basal plane

dislocations (BPDs) from the substrate into the epilayer [6, 7]. BPD's are defects that nucleate stacking faults under electrical stress that result in increased forward voltage drop and thus degradation/failure in bipolar devices/circuits [8].

A majority of BPD's ~70-80% spontaneously convert to relatively benign threading edge dislocations (TEDs) during epitaxial growth[9, 10]. Processes for successful elimination of BPDs (~99%) have been demonstrated for off-oriented substrates by the method of BPD-TED conversion[11] that relies on the exposure of the <0001> 4H-SiC basal plane (see equation 1 below) near the BPD by either KOH/Eutectic, or H₂ etching [12]. While these techniques are effective, they require multiple growths, etching and cleaning steps, adding complexity and cost to the epitaxial growth process.

However, a simpler solution to produce BPD free epilayers would be to directly use nearly on-axis or low offcut (tilt angle $\leq 1^\circ$) substrates for epi-growth. These substrates (offcut $\leq 1^\circ$) have very low BPD concentration due to the very less tilt in the basal plane (0001 plane) resulting in high conversion ratio of substrate BPDs into energetically favorable TEDs on the epilayer. As explained by Klapper and Küppers [13], BPD to TED conversion happens according to the following equation:

$$W = \frac{E}{\cos \alpha} \quad (1)$$

Where, W is the elastic energy of the dislocation per unit growth length, E is the elastic energies per unit length of dislocation line, α is the angle between the dislocation line and the growth direction i.e., $\alpha = 90 - \text{offcut angle}$ [10]. With a reduction in the offcut angle, W_{BPD} increases while W_{TED} reduces. The elastic energies per unit length of dislocation line for BPDs and TEDs were found to be almost the same, i.e., $E_{\text{BPD}} \sim E_{\text{TED}}$ [14] and we get $W_{\text{BPD}} \gg W_{\text{TED}}$. Hence it is energetically favorable for a BPD to get converted into a TED during epitaxial growth on a low

offcut substrate [10]. But the challenge in growing homoepitaxial layers on ideally on-axis or low vicinality (basal) surfaces is the difficulty to maintain 4H-SiC polytype uniformity due to the inclusion of thermodynamically favored cubic 3C-SiC polytype in the growth process [15 -17]. This is due to the lower density of steps on the surface, so that the adatoms on the surface only see the $\langle 0001 \rangle$ basal plane template, which reveals no stacking sequence, thereby initiating the nucleation of the thermodynamically favorable 3C polytype. This is opposed to the $\langle 1120 \rangle$ or $\langle 1100 \rangle$ faces at the step edges, which do reveal the stacking structure described above, enabling homoepitaxy. Thus, good homoepitaxial growth is achieved by the minimization of terrace nucleation of 3C-SiC, and maximizing step-flow growth.

Good 4H-SiC homoepitaxial growth can be achieved by i) Increasing temperature to encourage desorption of growth species from the terrace surfaces, although this can also reduce growth rate by increasing desorption from step-sites; ii) by using off-cut substrates as discussed above and iii) by changing the chemistry of the CVD process, which in turn affects the surface kinetics, thereby breaking certain inherent tradeoffs in the growth[18]. Previous studies have used this method to varying degrees of success[19], particularly with the addition of halogens to the growth to increase the volatility of growth species on the terrace surfaces. Previous studies have focused on the use of Cl-based chemistries (see below). While F-based chemistries are expected to offer improvements[20], a systematic study of on-axis growth has not been performed.

Qualitative studies in understanding the mechanism of 4H-SiC homoepitaxial growth on Si-face of ideally on-axis (step-free surfaces) and vicinal surfaces have been conducted previously. In-situ surface preparation techniques, growth parameters and growth temperature play a vital role in maintaining the polytype uniformity in on axis epilayers free of BPDs [17]. Hassan et al [17], Leone et al [21] demonstrated that high quality 4H-SiC homoepitaxial layers could be grown using Cl-based CVD. However, in their process, the dominant growth mode was spiral growth,

rather than step-flow growth, leading to degradation of morphology, and potentially increasing the likelihood of 3C nucleation and rough surfaces. For ideally on-axis substrates the growth mode is dominated by the spiral growth provided by the screw dislocations intersecting the surface[22]. Earlier studies showed that the spiral growth mode of on-axis epilayers has a strong dependence on C/Si ratio, with lower C/Si ratios favoring step-flow growth, and higher C/Si ratios favoring spiral growth that degrades the surface morphology, and can eventually lead to 3C nucleation[23]. There can also be terrace 3C nucleation at low temperatures, and nucleation at spiral growth sites. This is mitigated by using higher temperature growth to encourage desorption of growth species from the terraces, although this also can lead to lower growth rates. Studies on hetero epitaxial growth of high quality 3C-SiC intentionally grown on 4H-SiC/6H-SiC on-axis (step free) surface[24] show that 3C-SiC nucleation is favored at temperatures significantly lower ($\sim 1300^{\circ}\text{C}$) than the typical homoepitaxy temperature $\sim 1600^{\circ}\text{C}$. Kimoto et al. [15] showed that judicious preparation of the SiC surface with HCl etching encouraged homoepitaxy, although polytype uniformity was still an issue. Clearly, there is a need for investigating the key growth parameters that govern homoepitaxy on on-axis substrates, and this study provides some additional understanding. In this paper, a novel method to grow high quality step flow mediated homoepitaxial layers on Si face of nominally on-axis ($\pm 0.5^{\circ}$) substrates with high polytype uniformity using TetraFluoroSilane (TFS) as the Si precursor is presented.

Experimental details

Highly N- type doped ($\sim 10^{19} \text{ cm}^{-3}$) 4H-SiC(0001) on-axis substrates from a 3" wafer from Cree Research Inc. was used in this work. Tilt angle ranged between $\pm 0.5^{\circ}$. The wafer was diced into 8 x 8 mm² samples. The substrates were degreased with organic solvents, de-oxidized with HF and rinsed with de-ionized water before being blown dry with Argon for growth. A Graphite susceptor with TaC coating was used as the sample holder[25]. TaC coating on graphite susceptor reduces the residual acceptor impurity (Boron) concentration present in graphite by

serving as a getter[26] by providing thermal stability to graphite at high temperatures. In-situ etching was carried at 1600°C with only H₂ at 10 slm and at 300 torr pressure[20].

Growths were performed for different C/Si ratios keeping the Si precursor (TFS) flow rate constant at 5 sccm and varying the C precursor (propane) flow rate. Previously, good epilayer growth on on-axis substrates was shown using TFS (10 sccm) only at a C/Si ratio of 0.3[27]. The polytype uniformity degraded dramatically above a C/Si ratio of 0.3 due to the combined effects of reduced etching and higher growth rates at higher C/Si ratios. The growth results reported in this paper were carried at a low TFS flow rate of 5 sccm and the temperature was maintained at 1600°C at 300 Torr pressure for 1 hour. H₂ (10 slm) was used as the carrier gas. The thickness of the epilayers were measured using the Fourier transform infrared reflectance (FTIR)[28]. Surface morphology of the epilayers was analyzed using Nomarski Optical Microscope (NOM) and tapping mode Atomic Force Microscope (AFM). Net doping concentrations of the epilayers were measured by mercury probe Capacitance- Voltage method[29]. Polytype uniformity ensures the quality of SiC homoepitaxial growth. To check the crystalline quality and polytype inclusions Raman analysis was performed[30]. The Raman spectra were obtained using a Jobin-Yvon Raman spectrometer equipped with a charge-coupled-detector array for emission at room temperature. The excitation was carried out at room temperature using a 632 nm He-Ne laser excitation source with 2 μm spot size with 500x objective.

Results and discussion:

1. Growth rate and net doping concentration Vs. C/Si ratio

The growth experiments were carried out at different C/Si ratios which were varied by keeping Si precursor (TFS) flow constant and varying the C precursor (Propane) flow during each growth. As shown in fig.1(a), the growth rate gradually increases with the increase in C/Si ratio, as opposed to the C-independence often seen with silane-based growth[31]. With Cl-based

growth, some C-dependence is seen, which saturates at higher C/Si ratios[19]. However, in this study, we observe two distinct growth regimes, one at $C/Si < 1.8$, which shows growth rate, $R_g \sim 6 \mu\text{m/hr}$, relatively independent of C/Si ratio, and a second at $C/Si > 1.8$, which shows an approximately linear dependence on C/Si ratio up to $\sim 14 \mu\text{m/hr}$. Thick epilayers ($> 20 \mu\text{m}$) can be achieved by increasing the duration of growth. All layers were specular, with varying degrees of polytype uniformity, which will be discussed in the following section.

These two growth regimes are also reflected in the C/Si dependence of the unintentional doping of these homoepitaxial layers (Fig. 1(b)). Site-competition[32] is clearly observed, with N-type net doping concentration, N_d ranging from $\sim 5 \times 10^{18} \text{ cm}^{-3}$ to $\sim 7.2 \times 10^{14} \text{ cm}^{-3}$ for $C/Si \sim 0.6$ to 2.5. In SiC epitaxy, C and N compete for the same site. Therefore, at low C/Si ratio, there is an undersupply of C, providing more sites for N-impurities in the ambient to enter the growing SiC crystal. At high C/Si, these sites are filled, minimizing N-incorporation, and eventually transitioning to p-type doping. Typically, the C/Si trend is monotonic, unlike the 2-regime behavior seen here for the growth rate. At $C/Si \text{ ratio} < 1.8$ (regime 1), typical site-competition is seen. However, at $C/Si > 1.8$ (regime 2), a significant weakening of this behavior is observed, indicating that there is additional supply of Si-species compensating for the additional carbon, despite the fact that the SiF_4 silicon precursor supply has been constant.

The inference of additional Si-supply is supported by the faster R_g , linear in C/Si, seen at $C/Si > 1.8$ (fig.1 (a)). This observation is consistent with previous observations that without the addition of carbon, SiF_4 does not decompose to liberate silicon species for growth[33], attributed to the extremely large Gibbs free energy change (ΔG) of $\sim 360 \text{ kcal/mol}$ required for the direct decomposition of SiF_4 to elemental Si (Table 1, equation 13). However, with the addition of carbon, pathways for elemental-Si liberation, with significantly smaller $\Delta G \sim 100\text{-}200 \text{ kcal/mol}$

(Table 1, equations 17-21) are activated, providing additional Si to the growth which is explained graphically in fig.2 below.

Figure.2 is a pictorial representation of the important growth reactions governing growth regimes 1 and 2. In regime 1 (fig.2 (b)), it is shown that the boundary layer (region formed just above the surface of the epilayer) near the growth surface is predominantly controlled by the etching reaction of TFS with the surface Si (table 1, equation 14) at low C/Si ratios (≤ 1.8). In regime 2 (fig.2 (c)), a Si liberation reaction (table 1, equation 17) occurring at high C/Si ratios (> 1.8) in the boundary layer is shown.

Moreover, this additional elemental Si will drive the spontaneous decomposition of SiC (Table 1 Equation 2, $\Delta G \sim 13 \text{ kcal/mol}$) backward which also slows down the etching of SiC by SiF₄ (Table 1, equation 14), which was shown to significantly accelerate the etching of SiC in the presence of Si (l) liberated from the SiC decomposition[33], thereby suppressing R_g . Further suppression of the SiC decomposition is offered by the additional carbon supply at high C/Si, driving Table 1 Equation 2 backward, also minimizing the liberation of elemental Si. Without free Si on the SiC surface, the etching reaction (Table 1, equation 14) $\text{SiF}_4 (\text{g}) + \text{Si} (\text{l}) \rightarrow \text{SiF}_2 (\text{g})$ is again suppressed at low C/Si. Therefore, the combination of reduced etching, and liberation of additional Si species by the additional reactions at higher C/Si both lead to the transition from regime 1 to regime 2 (Fig 1(a)). While this analysis has been done for the liberation of elemental Si, there will certainly be additional more complex reaction pathways at high C/Si leading to the liberation of additional SiF₂, which will also drive the etching reaction 14 backward, again giving the same behavior. Further numerical simulations of the growth process are required to establish the key controlling reactions, although the morphological and polytype observations in the following suggest that elemental Si might be responsible.

2. Raman Analysis

Characteristic Raman spectra of 4H and 3C-SiC polytypes are shown in fig. 3(a) and (b) respectively. As reported by Nakashima and Haima [30], the phonon modes of interest in 4H-SiC include planar folded transverse optic (FTO) modes at 776 and 796 cm^{-1} , respectively and an axial folded longitudinal optic (FLO) mode at 964 cm^{-1} . For cubic SiC (3C-SiC) a dominant TO mode is at 796 cm^{-1} and an axial LO mode at 972 cm^{-1} (fig. 3(b)). For all the samples, the 4H-SiC characteristic (FTO and FLO) peaks were visible at 776 to 780 cm^{-1} and ~ 979 to 967 cm^{-1} (fig. 3(a)). The red shift (decrease in wavenumber) observed for FLO peaks with increasing C/Si ratio is as reported by Yugami et al [34] and is attributed to the impurity (doping) concentration which decreases as the C/Si ratio increases (fig. 3(c)).

The large difference in the wave number values between C/Si = 0.6 and C/Si = 1.0 is due to the large difference in doping concentration between those ratios. As reported by Yugami et al [34], the frequency of FLO band increases rapidly for carrier concentration above $5 \times 10^{17} \text{ cm}^{-3}$ and show less variation for carrier concentration below $1 \times 10^{17} \text{ cm}^{-3}$. As the net doping concentration decreases with increase in the C/Si ratio the Full Width Half Maximum (FWHM) of the 4H-FLO peaks also decreases (fig.3(d)). This is due to the collective excitation of the free carriers (plasmons) interacting with the longitudinal optical phonons to form LO phonon-plasmon coupled modes (LOPC) which is termed as FLO peak. The FWHM of 4H-FLO peak is sensitive to the change in free carrier density (doping concentration) as the Raman scattering process is governed by the electro-optic (EO), deformation potential (DP) and charge density fluctuation (CDF) at LOPC mode [30].

The intensity ratio values of 4H-FTO peak to 3C-FTO peak which is a measure to evaluate polytype uniformity is given in fig.4. Varying degrees of polytype uniformity were observed for epilayers grown at different C/Si ratios. From the ratio of peaks, it can be observed that the epilayer regions with negligible 3C inclusion have 4H/3C ratio >15 and for regions with

significant 3C inclusions the intensity ratio was found to be < 5 . For C/Si ratios < 1 and ≥ 2 the Raman 4H/3C peak ratio > 15 was found for the entire epilayer surface suggesting a better polytype uniformity of the epilayer. For C/Si ratios 1.0 to 1.8, the 4H/3C ratio varied throughout the surface of the epilayer indicating a poor polytype uniformity of the epilayer.

3. Surface morphology

From fig. 4, it is evident that the morphology of the epilayers shifts from a wavy step-flow at low C/Si ~ 0.6 , to a combination of island/spiral growth with step-flow growth at $1 < \text{C/Si} < 1.8$, then back to pure step flow at high C/Si > 1.8 . These regimes correspond with the R_g and doping regimes outlined above, further strengthening the argument that new chemical pathways have been activated at C/Si > 1.8 .

For the epilayers grown using TFS at 5 sccm, at low C/Si ~ 0.6 , the epilayer shows wavy step flow growth throughout the surface with few small spirals (fig.4 (a)). Very few screw dislocations emerging from the substrate are seen on the epilayer. At low C/Si conditions, step-flow growth is observed due to the suppressed nucleation process on the terrace enabling flow of steps. This happens due to enhanced surface etching at Si rich conditions (Table 1- equations 1, 14). Increased surface etching minimizes the probability of nuclei attaching to the terrace making it energetically less favorable and thus suppressing the spiral growth [22]. Waviness on the surface steps (fig.4 (a)) is attributed to the presence of step bunching often observed on substrates with smaller offcuts (i.e. 4°)[33].

With the increase in C/Si (Fig 4(b-d)), increase in the 3C inclusions (spiral and island growth) on the epilayer surface is observed. As the C/Si ratio increases, availability of C in the boundary layer (formed just above the surface of the epilayer) increases. This mitigates the surface etching reaction rate of SiF_4 on Si (Table 1- equation 14) due to the hindrance offered by the cluster of C atoms present near the surface for the reaction between SiF_4 and Si atoms on the surface resulting in slow etching[35]. Thus 2D nucleation rate for 3C polytype inclusion becomes more

than the surface adatoms desorption rate. It has been calculated that at high carbon partial pressure (elemental C availability) and at lower growth temperature the thermodynamic stability of the 3C polytype is higher than any other SiC polytypes[36]. It is also speculated that carbon species adhere better on a flat surface (on-axis or low vicinality substrates) and Silicon species diffuse in the gas phase more slowly than carbon species due to their larger molecular weight [36], especially through the boundary layer. Increase in C/Si reduces the desorption capacity of C atoms (on flat surfaces) from the surface thereby increasing carbon supersaturation near the surface favoring 3C inclusions[23]. The evidence for lower off-angle substrate epitaxial layers being “carbon rich” is reported both by Huh et al.[37] and Yamamoto et al.[38]. The experimental data for doping (fig.1 (b)) agrees with the above statement where doping concentration (Nitrogen incorporation) decreases at these C/Si ratios (1, 1.5, 1.8), which is in accordance with the site-competition-epitaxy theory[32].

An interesting feature is observed at very high C/Si (>1.8) (fig.1 (a) -Regime 2) with the surface morphology shifting back to uniform step flow growth without any 3C inclusions (fig. 4(e), (f)). As discussed earlier, abundant supply of Carbon at ratios ≥ 2.0 liberates additional Si in the gas phase (Table 1, equations 17-21). Non-saturating increase in R_g (fig.1 (a)) and low n-type doping concentration (restricting p-type) (fig.1 (b)) serves as a strong evidence of elemental Si liberation at $C/Si \geq 2$. It is found that 4H-SiC is more stable at high C/Si as hexagonal polytype is favored at C rich conditions[35] whereas 3C-SiC is more stable at low temperature and occur at high supersaturation conditions as observed and explained for $1 \leq C/Si \leq 1.8$. Thus the suppression of 3C inclusions in growth regime 2 ($C/Si \geq 2$) happens due to the combined effects of C-rich condition additionally liberating gas phase Si that lowers C supersaturation near the growth surface favoring 4H-SiC formation[35].

Typically, nearly on-axis epilayers with no 3C inclusions show uniform spiral growth[22, 23]. But the epilayers grown at $C/Si \geq 2$ reported in this paper exhibit uniform step flow growth (fig 1(a) -Regime 2). The reason for this prominent change in surface morphology is due to several C-reactions that liberate elemental Si (fig.2 and Table 1- equations 17 to 21) at the high growth temperature (1600 °C) as discussed earlier in this paper. On a nearly on-axis substrate, a regular array of steps is present. Spirals are formed as a result of revolution of pinned steps created by dislocations merging at a surface[39]. Due to the step line tension, there is a critical curvature (ρ_c) above which a spiral grows[22]. If the growth velocity of a straight step is V_{step} , the angular velocity of spiral ω is given by [40]

$$\omega \approx 0.33V_{step}/\rho_c \quad (2)$$

Accordingly, the time required for one turn of spiral is,

$$T = \frac{2\pi}{\omega} \approx \frac{19\rho_c}{V_{step}} \quad (3)$$

If the time taken for straight steps (t) is faster than the time taken by spiral steps (T), i.e., when $t < T$, a spiral will not form. Using the simple surface diffusion model proposed by Kimoto et al[41], step-flow growth rate is given by,

$$R_g = V_{step} \tan\theta \quad (4)$$

Where V_{step} is the step velocity and θ is the off-angle of a substrate ($\sim 0.5^\circ$). Since R_g increases almost linearly for $C/Si \geq 2$ (fig.1 (a) regime 2) compared to that of $C/Si < 2$ (fig.1 (a) regime 1), the straight step velocity with increasing R_g overcomes the spiral step velocity suppressing the spiral growth at $C/Si \geq 2$. Thus increase in R_g due to extra Si that is liberated during the growth reactions at $C/Si \geq 2$ influences step flow growth and suppresses spiral growth.

Conclusion

Homoepitaxial growth on nearly on-axis 4H-SiC using a novel Si precursor at low flow rates (5 sccm) has been reported. The grown epilayers exhibit good polytype uniformity at low and high

C/Si ratios. A two regime growth model is reported. A novel growth regime is identified at C rich conditions and new reaction pathways are highlighted to obtain uniform step flow growth of on-axis epilayers with low surface roughness ($\sim 1\text{nm}$). The homoepitaxial growth reported in this paper opens up the possibility of achieving BPD free on-axis epilayers with high 4H polytype uniformity (regime 2) and also with varying degrees of 3C polytype inclusions (regime 1). Epilayers with growth rate ranging from low ($5\mu\text{m/hr}$) to a maximum of $\sim 15\mu\text{m/hr}$ (step flow) is reported which can be extensively used for fabricating high power devices free of BPDs.

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References:

- [1] J.B. Casady, R.W. Johnson, Status of silicon carbide (SiC) as a wide-bandgap semiconductor for high-temperature applications: A review, *Solid. State. Electron.* 39 (1996) 1409–1422. doi:10.1016/0038-1101(96)00045-7.
- [2] M.E. Levinshtein, S.L. Rumyantsev, M.S. Shur, *Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, SiC, SiGe*, John Wiley & Sons, 2001.
- [3] A. Qteish, V. Heine, R.J. Needs, Polarization, band lineups, and stability of SiC polytypes, *Phys. Rev. B.* 45 (1992) 6534–6542. doi:10.1103/PhysRevB.45.6534.

- [4] H. Matsunami, T. Kimoto, Step-controlled epitaxial growth of SiC: High quality homoepitaxy, *Mater. Sci. Eng. R Reports*. 20 (1997) 125–166. doi:10.1016/S0927-796X(97)00005-3.
- [5] M. Treu, R. Rupp, H. Brunner, F. Dahlquist, C. Hecht, Challenges and First Results of SiC Schottky Diode Manufacturing using a 3-Inch Technology, *Mater. Sci. Forum*. 457-460 (2004) 981–984. doi:10.4028/www.scientific.net/MSF.457-460.981.
- [6] P. Bergman, H. Lendenmann, P.Å. Nilsson, U. Lindefelt, P. Skytt, Crystal Defects as Source of Anomalous Forward Voltage Increase of 4H-SiC Diodes, *Mater. Sci. Forum*. 353-356 (2001) 299–302. doi:10.4028/www.scientific.net/MSF.353-356.299.
- [7] H. Lendenmann, F. Dahlquist, N. Johansson, R. Söderholm, P.Å. Nilsson, P. Bergman, et al., Long Term Operation of 4.5kV PiN and 2.5kV JBS Diodes, *Mater. Sci. Forum*. 353-356 (2001) 727–730. doi:10.4028/www.scientific.net/MSF.353-356.727.
- [8] M. Skowronski, S. Ha, Degradation of hexagonal silicon-carbide-based bipolar devices, *J. Appl. Phys.* 99 (2006) 011101. doi:10.1063/1.2159578.
- [9] Z.H. Zhang, A. Shrivastava, T.S. Sudarshan, Why Are Only Some Basal Plane Dislocations Converted to Threading Edge Dislocations During SiC Epitaxy?, *Mater. Sci. Forum*. 527-529 (2006) 419–422. doi:10.4028/www.scientific.net/MSF.527-529.419.
- [10] Z. Zhang, T.S. Sudarshan, Basal plane dislocation-free epitaxy of silicon carbide, *Appl. Phys. Lett.* 87 (2005) 151913. doi:10.1063/1.2093931.
- [11] H. Song, T.S. Sudarshan, Basal plane dislocation conversion near the epilayer/substrate interface in epitaxial growth of 4° off-axis 4H-SiC, *J. Cryst. Growth*. 371 (2013) 94–101. doi:10.1016/j.jcrysgro.2013.02.011.
- [12] R.L. Myers-Ward, B.L. VanMil, R.E. Stahlbush, S.L. Katz, J.M. McCrate, S.A. Kitt, et al., Turning of Basal Plane Dislocations during Epitaxial Growth on 4° Off-Axis 4H-SiC,

- Mater. Sci. Forum. 615-617 (2009) 105–108. doi:10.4028/www.scientific.net/MSF.615-617.105.
- [13] H. Klapper, H. Küppers, Directions of dislocation lines in crystals of ammonium hydrogen oxalate hemihydrate grown from solution, *Acta Crystallogr. Sect. A*. 29 (1973) 495–503. doi:10.1107/S0567739473001257.
 - [14] T. Ohno, H. Yamaguchi, S. Kuroda, K. Kojima, T. Suzuki, K. Arai, Direct observation of dislocations propagated from 4H–SiC substrate to epitaxial layer by X-ray topography, *J. Cryst. Growth*. 260 (2004) 209–216. doi:10.1016/j.jcrysgro.2003.08.065.
 - [15] S. Nakamura, T. Kimoto, H. Matsunami, Homoepitaxy of 6H–SiC on nearly on-axis (0001) faces by chemical vapor deposition Part I: Effect of C/Si ratio on wide-area homoepitaxy without 3C–SiC inclusions, *J. Cryst. Growth*. 256 (2003) 341–346. doi:10.1016/S0022-0248(03)01385-X.
 - [16] C. Hallin, Q. Wahab, I.G. Ivanov, P. Bergman, E. Janzén, Homoepitaxial On-Axis Growth of 4H- and 6H-SiC by CVD, *Mater. Sci. Forum*. 457-460 (2004) 193–196. doi:10.4028/www.scientific.net/MSF.457-460.193.
 - [17] J. Hassan, J.P. Bergman, A. Henry, E. Janzén, On-axis homoepitaxial growth on Si-face 4H–SiC substrates, *J. Cryst. Growth*. 310 (2008) 4424–4429. doi:10.1016/j.jcrysgro.2008.06.081.
 - [18] T.S. Sudarshan, T. Rana, H. Song, M.V.S. Chandrashekhara, Trade-Off between Parasitic Deposition and SiC Homoepitaxial Growth Rate Using Halogenated Si-Precursors, *ECS J. Solid State Sci. Technol.* 2 (2013) N3079–N3086. doi: 10.1149/2.017308jss.
 - [19] H. Song, T. Rana, M.V.S. Chandrashekhara, S.U. Omar, T.S. Sudarshan, Comparison of SiC epitaxial growth from dichlorosilane and tetrafluorosilane precursors, *ECS Trans.* 58 (2013) 97–109. doi: 10.1149/05804.0097ecst.

- [20] T. Rana, M.V.S. Chandrashekhar, T.S. Sudarshan, Elimination of silicon gas phase nucleation using tetrafluorosilane (SiF_4) precursor for high quality thick silicon carbide (SiC) homoepitaxy, *Phys. Status Solidi.* 209 (2012) 2455–2462. doi:10.1002/pssa.201228319.
- [21] S. Leone, H. Pedersen, A. Henry, O. Kordina, E. Janzén, Homoepitaxial Growth of 4H-SiC on On-Axis Si-Face Substrates Using Chloride-Based CVD, *Mater. Sci. Forum.* 600-603 (2009) 107–110. doi:10.4028/www.scientific.net/MSF.600-603.107.
- [22] S. Nakamura, T. Kimoto, H. Matsunami, Effect of C/Si Ratio on Spiral Growth on 6H-SiC (0001), *Jpn. J. Appl. Phys.* 42 (2003) L846. doi: 10.1143/JJAP.42.L846.
- [23] S. Leone, H. Pedersen, A. Henry, O. Kordina, E. Janzén, Thick homoepitaxial layers grown on on-axis Si-face 6H- and 4H-SiC substrates with HCl addition, *J. Cryst. Growth.* 312 (2009) 24–32. doi:10.1016/j.jcrysgr.2009.10.011.
- [24] P.G. Neudeck, A.J. Trunek, D.J. Spry, J.A. Powell, H. Du, M. Skowronski, et al., CFD Growth of 3C-SiC on 4H/6H Mesas, (2006). doi:10.1002/cvde.200506460.
- [25] B.E. Landini, Susceptor effects on the morphological and impurity properties of 4H-SiC epilayers, *J. Electron. Mater.* 29 (n.d.) 384–390. doi:10.1007/s11664-000-0082-8.
- [26] M.G. Spencer, SiC fabrication technology: growth and doping, *SiC Mater. Devices.* 52 (1998) 21.
- [27] T. Rana, High Quality Silicon Carbide Epitaxial Growth by Novel Fluorosilane Gas Chemistry For Next Generation High Power Electronics, (2013), p.142 (Doctoral Dissertation). Retrieved from <http://scholarcommons.sc.edu/etd/2432>.
- [28] S. Sunkari, M.S. Mazzola, J.P. Mazzola, H. Das, J.L. Wyatt, Investigation of longitudinal-optical phonon-plasmon coupled modes in SiC epitaxial film using fourier transform infrared reflection, *J. Electron. Mater.* 34 (n.d.) 320–323. doi:10.1007/s11664-005-0103-8.

- [29] H.J. Kim, R.F. Davis, Theoretical and Empirical Studies of Impurity Incorporation into β -SiC Thin Films during Epitaxial Growth, *J. Electrochem. Soc.* 133 (1986) 2350–2357. doi: 10.1149/1.2108406.
- [30] S. Nakashima, H. Harima, Raman Investigation of SiC Polytypes, *Phys. Status Solidi.* 162 (1997) 39–64. doi:10.1002/1521-396X(199707)162:1<39::AID-PSSA39>3.0.CO;2L.
- [31] W. Chen, M.A. Capano, Growth and characterization of 4H-SiC epilayers on substrates with different off-cut angles, *J. Appl. Phys.* 98 (2005) 114907. doi: 10.1063/1.2137442.
- [32] D.J. Larkin, P.G. Neudeck, J.A. Powell, L.G. Matus, Site-competition epitaxy for superior silicon carbide electronics, *Appl. Phys. Lett.* 65 (1994) 1659. doi:10.1063/1.112947.
- [33] T. Rana, M.V.S. Chandrashekhar, T.S. Sudarshan, Vapor phase surface preparation (etching) of 4H-SiC substrates using tetrafluorosilane (SiF₄) in a hydrogen ambient for SiC epitaxy, *J. Cryst. Growth.* 380 (2013) 61–67. doi:10.1016/j.jcrysgro.2013.05.030.
- [34] H. Yugami, S. Nakashima, A. Mitsuishi, A. Uemoto, M. Shigeta, K. Furukawa, et al., Characterization of the free-carrier concentrations in doped β -SiC crystals by Raman scattering, *J. Appl. Phys.* 61 (1987) 354. doi:10.1063/1.338830.
- [35] A. Fissel, Thermodynamic considerations of the epitaxial growth of SiC polytypes, *J. Cryst. Growth.* 212 (2000) 438–450. doi:10.1016/S0022-0248(00)00330-4.
- [36] Ö. Danielsson, A. Henry, E. Janzén, Growth rate predictions of chemical vapor deposited silicon carbide epitaxial layers, *J. Cryst. Growth.* 243 (2002) 170–184. doi:10.1016/S0022-0248(02)01486-0.
- [37] S.W. Huh, H.J. Chung, S. Nigam, A.Y. Polyakov, Q. Li, M. Skowronski, et al., Residual impurities and native defects in 6H-SiC bulk crystals grown by halide chemical-vapor deposition, *J. Appl. Phys.* 99 (2006) 013508. doi:10.1063/1.2150593.

- [38] T. Yamamoto, T. Kimoto, H. Matsunami, Impurity Incorporation Mechanism in Step-Controlled Epitaxy Growth Temperature and Substrate Off-Angle Dependence, *Mater. Sci. Forum.* 264-268 (1997) 111–114. doi:10.4028/www.scientific.net/MSF.264-268.111.
- [39] W.-K. Burton, N. Cabrera, F.C. Frank, The growth of crystals and the equilibrium structure of their surfaces, *Philos. Trans. R. Soc. London A Math. Phys. Eng. Sci.* 243 (1951) 299–358. doi:10.1098/rsta.1951.0006
- [40] E. Budevski, G. Staikov, V. Bostanov, Form and step distance of polygonized growth spirals, *J. Cryst. Growth.* 29 (1975) 316–320. doi:10.1016/0022-0248(75)90178-5.
- [41] T. Kimoto, H. Matsunami, Surface kinetics of adatoms in vapor phase epitaxial growth of SiC on 6H-SiC{0001} vicinal surfaces, *J. Appl. Phys.* 75 (1994) 850. doi:10.1063/1.356439.

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Figure 1 (a) & (b) : Single Column image

Figure.1: On-axis growth results using TFS (5 sccm) (a) R_g vs. C/Si ratio curve, (b) Unintentional doping concentration vs. C/Si ratio curve (trend lines shown in 1.(a) & (b) are guide to the eyes)

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Figure 4: (a) till (e) 1.5 column images

(b) C/Si ratio = 1.0

Raman intensity ratio:

$$\frac{4H - FTO}{3C - FTO} = 2.3$$

Raman intensity ratio:

$$\frac{4H - FTO}{3C - FTO} = 18.5$$

(c) C/Si ratio = 1.5

Raman intensity ratio:

$$\frac{4H - FTO}{3C - FTO} = 3.8$$

Raman intensity ratio:

$$\frac{4H - FTO}{3C - FTO} = 22.6$$

(d) C/Si ratio = 1.8

Raman intensity ratio:

$$\frac{4H - FTO}{3C - FTO} = 3.5$$

Raman intensity ratio:

$$\frac{4H - FTO}{3C - FTO} = 4.2$$

Figure.4: NOM images (100x magnification) and AFM images ($5 \times 5 \mu\text{m}^2$) of nearly on-axis epilayers grown using TFS (5 sccm). (a) C/Si = 0.6, $R_g = 5.6 \mu\text{m/h}$, (b) C/Si = 1.0, $R_g = 5.8 \mu\text{m/h}$, (c) C/Si = 1.5, $R_g = 7.2 \mu\text{m/h}$, (d) C/Si = 1.8, $R_g = 6.3 \mu\text{m/h}$, (e) C/Si = 2.0, $R_g = 9.2 \mu\text{m/h}$, (f) C/Si = 2.5, $R_g = 14.4 \mu\text{m/h}$

Table 1: Single column image

	Reaction	1800 K	1900 K
Dissociation and evaporation reactions			
1	$\text{SiC(s)} \rightarrow \text{Si(s)} + \text{C(s)}$	13.72	13.53
2	$\text{SiC(s)} \rightarrow \text{Si(l)} + \text{C(s)}$	12.90	12.00
3	$\text{SiC(s)} \rightarrow \text{Si(g)} + \text{C(s)}$	58.19	54.60
4	$\text{SiC(s)} \rightarrow 1/2\text{Si}_2\text{C(g)} + 1/2\text{C(s)}$	36.99	34.69
5	$\text{Si(l)} \rightarrow \text{Si(g)}$	45.29	42.59
Hydrogen reactions			
6	$\text{SiC(s)} + 1/2\text{H}_2\text{(g)} \rightarrow \text{Si(g)} + 1/2\text{C}_2\text{H}_2\text{(g)}$	73.44	69.23
7	$\text{Si(l)} + 1/2\text{H}_2 \rightarrow \text{SiH(g)}$	44.81	43.12
8	$\text{Si(l)} + 2\text{H}_2\text{(g)} \rightarrow \text{SiH}_4\text{(g)}$	48.96	52.02
9	$\text{C(s)} + 3/2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{(g)}$	42.86	43.47
10	$\text{C(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)}$	25.94	28.62
11	$2\text{C(s)} + \text{H}_2\text{(g)} \rightarrow \text{C}_2\text{H}_2\text{(g)}$	30.50	29.26
12	$2\text{C(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{C}_2\text{H}_4\text{(g)}$	44.34	46.34
Halogen reactions			
13	$\text{SiF}_4 \rightarrow \text{Si(g)} + 2\text{F}_2$	368.90	362.20
14	$\text{Si(l)} + \text{SiF}_4 \rightarrow 2\text{SiF}_2\text{(g)}$	19.69	15.93
15	$\text{SiH}_2\text{Cl}_2 \rightarrow \text{Si(g)} + 2\text{HCl}$	30.17	24.21
16	$\text{Si(l)} + 2\text{HCl} \rightarrow \text{SiCl}_2 + \text{H}_2$	-4.06	-3.79
17	$\text{C(s)} + 1/4\text{SiF}_4 \rightarrow \text{CF} + 1/4\text{Si(g)}$	107.83	103.65
18	$\text{C(s)} + 1/2\text{SiF}_4 \rightarrow \text{CF}_2 + 1/2\text{Si(g)}$	128.23	124.16
19	$4\text{C(s)} + 3\text{SiF}_4 \rightarrow 4\text{CF}_3 + 3\text{Si(g)}$	184.63	180.62
20	$\text{C(s)} + \text{SiF}_4 \rightarrow \text{CF}_4 + \text{Si(g)}$	211.04	206.36
21	$2\text{C(s)} + 1/2\text{SiF}_4 \rightarrow \text{C}_2\text{F}_2 + 1/2\text{Si(g)}$	175.24	171.05

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