

# Low-temperature homoepitaxial growth of 4H–SiC with CH<sub>3</sub>Cl and SiCl<sub>4</sub> precursors

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## ABSTRACT

In prior research, a possibility to increase the growth rate of the low-temperature epitaxial growth of 4H–SiC was explored by supplementing chloro-carbon precursor CH<sub>3</sub>Cl with HCl as an additional source of chlorine. In the current work, SiCl<sub>4</sub> was investigated as a replacement for SiH<sub>4</sub>+HCl. The homogeneous nucleation in the gas phase was further reduced compared to SiH<sub>4</sub>+HCl growth, thus essentially eliminating the main bottleneck for increasing the growth rate ( $R_g$ ). However, for low values of the carrier gas flow, premature dissociation of Si gas-phase clusters was found to cause  $R_g$  non-homogeneity and triangular defect formation. The drastically suppressed homogeneous nucleation opened the window for increasing the carrier gas flow velocity in order to improve the  $R_g$  homogeneity from upstream to downstream. Nevertheless, generation of triangular defects was significant at  $R_g$  above 5–6  $\mu\text{m}/\text{h}$ . The process window for obtaining good epilayer morphology was found to correspond to Si supply-limited mode. The window was restricted at low values of C/Si ratio by formation of Si-rich islands/droplet and at high C/Si ratio by formation of polycrystalline SiC. The process window became increasingly narrower at higher  $R_g$ , which serves as a new bottleneck for significantly increasing  $R_g$  at such low growth temperatures.

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## 1. Introduction

Commercial silicon carbide (SiC) devices have become increasingly important for high-power and high voltage applications [1,2]. High epitaxial growth rates ( $R_g$ ) are required for manufacturing high-power SiC devices. High growth temperatures ( $> 1500^\circ\text{C}$ ) and substrates with large off-axis angles have long been used to ensure favorable surface reaction mechanisms.

In contrast to the traditional epitaxial techniques relying on high temperatures, step-flow growth on 8-degree off-axis substrates was demonstrated by the authors' group at temperatures as low as  $1300^\circ\text{C}$  by employing chloro-carbon precursor CH<sub>3</sub>Cl replacing the traditional propane [3]. However,  $R_g$  of only 2–3  $\mu\text{m}/\text{h}$  without significant morphology degradation could be achieved at  $1300^\circ\text{C}$ , which was due to homogeneous nucleation of Si in the gas phase restricting supply of Si ad-species to the growth surface [4].

With respect to the regular high growth temperatures, homogeneous nucleation of Si was also recognized as a significant obstacle to achieving higher  $R_g$ . Multiple groups successfully employed addition of HCl during the regular-temperature epitaxial growth for addressing the Si vapor condensation

problems [5,6]. Subsequently, qualitatively similar improvements were achieved by using chlorinated silicon precursors (e.g., trichlorosilane and methyltrichlorosilane) [7,8]. Growth rates in excess of 100  $\mu\text{m}/\text{h}$  were demonstrated at  $1570^\circ\text{C}$  [9]. The role of different chlorinated species was evaluated using classical nucleation theory and quantum mechanical refinement [10]. Theoretical calculations suggested that the gas-phase chemistry should be significantly influenced by the addition of chlorine-containing species [10,11].

The benefits of having more chlorine participating in chemical reactions were also explored in the low-temperature epitaxial growth. The amount of the beneficial Cl-containing products of CH<sub>3</sub>Cl decomposition was found insufficient to eliminate the homogeneous nucleation. Therefore HCl addition was used [12]. As expected, formation of Si clusters was significantly suppressed in the presence of HCl even at  $1300^\circ\text{C}$ . However, it was established that the influence of HCl is more complicated and not exclusively beneficial. The magnitude of  $R_g$  increase was found to be less significant than what was expected from the apparent degree of the gas clusters dissociation enhanced by HCl. Also, significant  $R_g$  non-homogeneity (steep  $R_g$  reduction from upstream to downstream) was observed even at the same  $\text{H}_2$  carrier gas flow velocities that provided nearly perfect  $R_g$  homogeneity without HCl. It was established that a new mechanism for precursors' depletion becomes important when Si gas-phase homogeneous nucleation is reduced by the HCl

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addition. With HCl, premature dissociation of the gas-phase clusters and premature release of silicon may cause depletion of the growth precursors by vigorous polycrystalline deposition in the upstream portion of the hot zone. This depletion was negligible without HCl due to Si absorption by gas-phase clusters keeping Si away from surface reactions. The depletion by polycrystalline deposition may significantly reduce the benefits of suppressing homogeneous nucleation at low temperature.

It is well known from the experience of Si epitaxial growth that chloro-silane precursors (when used instead of  $\text{SiH}_4$ ) allow significant reduction of the homogeneous nucleation [13]. This happens due to domination of  $\text{SiCl}_2$  species, which are less susceptible to cluster formation in the gas phase. Silicon tetrachloride precursor ( $\text{SiCl}_4$ ) was successfully used for SiC growth (so called halide-CVD technique). However, it was conducted at much higher growth temperatures (above  $2000^\circ\text{C}$ ), which is required for bulk growth using the high-temperature CVD technique [14]. It is also known that chloro-silane precursors exhibit slower kinetics of the dissociation reactions.

In this work, chlorinated silicon precursor  $\text{SiCl}_4$  was investigated and compared to  $\text{SiH}_4+\text{HCl}$  as a source of additional chlorine to suppress the homogeneous nucleation, while avoiding premature release of silicon from the silicon precursor. While certain undesirable aspects of the growth behavior were found qualitatively similar to  $\text{SiH}_4+\text{HCl}$  growth, further process optimization allowed overcoming at least some problems coming from premature dissociation of Si clusters in the gas phase.

## 2. Experimental

Commercial 4H-SiC wafers cut  $8^\circ$  off-axis towards the  $[1\ 1\ \bar{2}\ 0]$  direction purchased from different manufacturers were used as substrates for epitaxial growth. Growth experiments were performed in a horizontal hot wall CVD reactor at 140 Torr and  $1300^\circ\text{C}$ . A SiC coated graphite susceptor was used. As in all of our previous low-temperature growth experiments, the SiC coating showed no sign of degradation during the growth at  $1300^\circ\text{C}$  even after a very prolonged use. Palladium membrane-purified  $\text{H}_2$  was used as a carrier gas. Chloromethane ( $\text{CH}_3\text{Cl}$ ) was used as the carbon source, which is the same carbon precursor as what was used in the previous studies of the low-temperature epitaxial growth [3,4]. New precursor silicon tetrachloride was used as the silicon source.

The epilayer thickness maps were obtained by reflective Fourier transform infrared spectroscopy (FTIR). The model fit of the experimental data was conducted over the range of wavenumber from  $1000$  to  $6000\text{ cm}^{-1}$ . The thickness was periodically confirmed by SIMS. The surface morphology was examined by Nomarski optical microscopy. Rigaku Ultima III powder X-ray diffractometer was used to analyze the relative contents of different phases in the polycrystalline deposits that were formed at different regions of the hot zone of the reactor as well as in the degraded epitaxial layers grown outside of the optimal process window.

## 3. Results and discussions

As was established in the previous work, formation of Si gas-phase clusters can be suppressed by adding HCl during the low-temperature epitaxial growth with  $\text{CH}_3\text{Cl}$  and  $\text{SiH}_4$  precursors [12]. The resulting enhanced supply of Si growth species causes an increase of  $R_g$ . However, this improvement is

spoiled by significant deterioration of the  $R_g$  homogeneity -  $R_g$  reduction from upstream to downstream (Fig. 1a, profile II).

Growth with  $\text{SiCl}_4$  produced qualitatively similar changes in  $R_g$  (Fig. 1a, profile III). The  $R_g$  was higher than  $R_g$  in  $\text{SiH}_4+\text{HCl}$  growth with the same flow of the silicon precursor, which is believed to be due to further suppressed homogeneous nucleation in the gas phase. This conclusion is supported by the absence of powder-like silicon deposits on the reactor walls downstream from the hot zone.

However, the expectation was not confirmed that slower dissociation of  $\text{SiCl}_4$  as compared to  $\text{SiH}_4+\text{HCl}$  should reduce precursor depletion caused by the polycrystalline deposition mechanism. A significant  $R_g$  reduction from upstream to downstream qualitatively similar to the  $\text{SiH}_4+\text{HCl}$  case was observed (Fig. 1a, profile III). Also, triangular defects accompanied increase of  $R_g$ , especially in the upstream portion of the growth zone, which is similar to what was previously reported for  $\text{SiH}_4+\text{HCl}$  growth. All three curves of Fig. 1a were obtained with  $\text{H}_2=1\text{ slm}$  (which corresponds to  $\text{Si}/\text{H}_2=0.024$ ) and  $\text{C}/\text{Si}=0.25$ .

### 3.1. $R_g$ non-homogeneity in epitaxial growth with $\text{SiCl}_4$ precursor

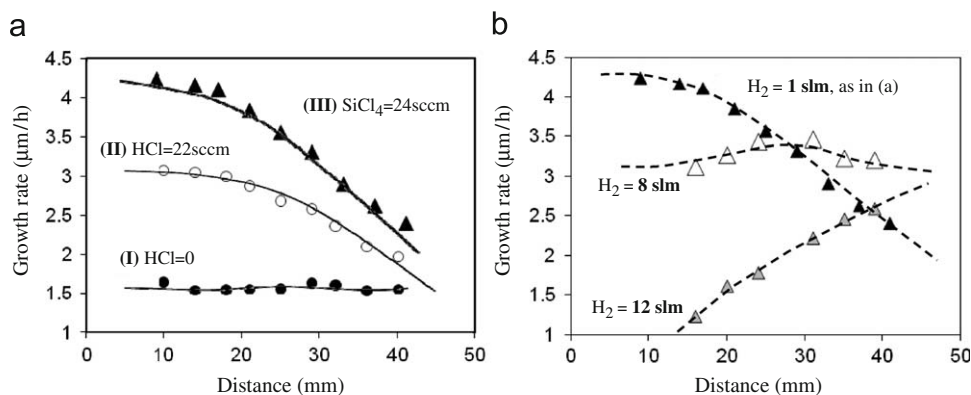
The origin of  $R_g$  non-homogeneity from upstream to downstream in low-temperature epitaxial growth with  $\text{SiCl}_4$  precursor (Fig. 1a, profile III) was analyzed. Fig. 2 shows surface morphology of SiC test-samples placed in the upstream portion of the hot zone at different distances from the leading edge of the growth zone. In all three growth runs of Fig. 2,  $\text{Si}/\text{H}_2=0.024$  and  $\text{C}/\text{Si}=0.25$ . Rows (1) and (2) of Fig. 2 compare results of the  $\text{CH}_3\text{Cl}+\text{SiH}_4$  growth ( $\text{SiH}_4=24\text{ sccm}$ ) with and without HCl addition, respectively [12]. As was described in the introduction, the  $R_g$  non-homogeneity in  $\text{SiH}_4+\text{HCl}$  growth at  $1300^\circ\text{C}$  was due to HCl-induced premature release of Si growth species from gas-phase clusters. Following this release of Si, the Si growth species get subsequently depleted by enhanced formation of Si-rich polycrystalline deposits (e.g., Figs. 2(c2–f2) compared to (c1–f1)).

The analysis of the polycrystalline deposits in the upstream portion of the hot zone reported in Ref. [12] was next extended to growth experiments with  $\text{SiCl}_4$  replacing the  $\text{SiH}_4+\text{HCl}$ , with the same  $\text{Si}/\text{H}_2=0.024$  and  $\text{C}/\text{Si}=0.25$  (Fig. 2(3)). The location along the gas-flow direction at which the polycrystalline deposition first appeared is significantly more downstream (closer to the growth zone) for  $\text{SiCl}_4$  (Fig. 2(c3)) as compared to  $\text{SiH}_4$  and  $\text{SiH}_4+\text{HCl}$  cases (Figs. 2(b1) and (b2)). This location corresponds to the onset of thermal decomposition of the corresponding Si precursor. As was expected,  $\text{SiCl}_4$  exhibits slower dissociation kinetics.

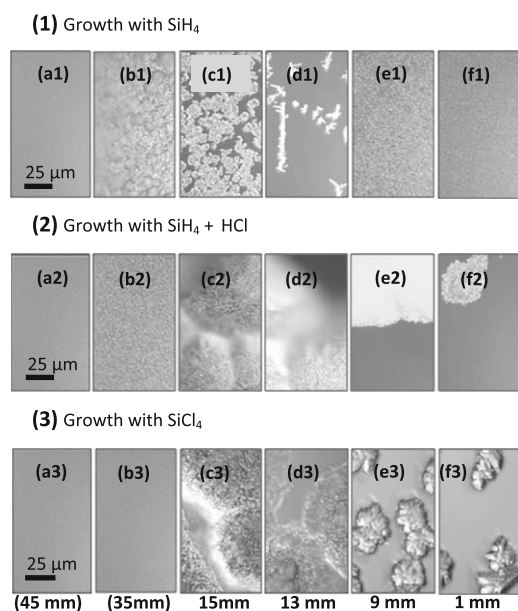
At more downstream locations of the hot zone, the polycrystalline deposition in  $\text{SiCl}_4$  experiments became similar to the  $\text{SiH}_4+\text{HCl}$  case, while different from the  $\text{SiH}_4$  growth without HCl. As was reported earlier for  $\text{SiH}_4$ -without-HCl process [12], polycrystalline islands quickly disappeared when approaching the hot susceptor (Figs. 2(c1, d1, etc.)). This was explained by homogeneous nucleation leading to the formation of low-diffusivity gas-phase clusters making Si unavailable for polycrystalline deposition. Suppressed formation of Si clusters when using  $\text{SiCl}_4$  resulted in significant polycrystalline deposition in region (c3) of Fig. 2. This is similar to the outcome of the growth with HCl addition (Fig. 2(c2)).

The polycrystalline deposition depletes a portion of Si growth species released from the clusters, thus limiting the  $R_g$  in the growth zone. Consequently, the mechanism of  $R_g$  non-homogeneity in  $\text{SiCl}_4$  growth is qualitatively similar to the  $\text{SiH}_4+\text{HCl}$  case.

More careful comparison showed that the polycrystalline deposition in the  $\text{SiCl}_4$  case is somewhat less significant but lasts



**Fig. 1.** (a) Growth rate ( $R_g$ ) at 1300 °C as a function of the distance from the leading edge of the growth zone: (I)  $\text{SiH}_4=24$  sccm without HCl, (II) the same  $\text{SiH}_4$  flow with HCl added, and (III)  $\text{SiH}_4+\text{HCl}$  is replaced with  $\text{SiCl}_4$ . (b) Optimization of the  $R_g$  homogeneity in the  $\text{SiCl}_4$  growth by increasing the  $\text{H}_2$  carrier gas flow.  $R_g$  profile is optimized at  $\text{H}_2=8$  slm.  $\text{H}_2$  flows of 8 and 12 slm allowed using much reduced  $\text{SiCl}_4$  flows (1 sccm) compared to  $\text{H}_2=1$  slm when using  $\text{SiCl}_4=24$  sccm for the same  $\text{CH}_3\text{Cl}=6$  sccm.

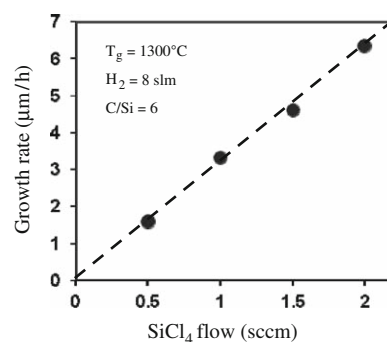


**Fig. 2.** Polycrystalline Si-rich deposits in the upstream regions of the hot zone: (1) growth with  $\text{SiH}_4$  without HCl, (2)  $\text{SiH}_4$  with  $\text{HCl}=24$  sccm ( $\text{Cl}/\text{Si}=1.09$ ), and (3)  $\text{SiCl}_4$  instead of  $\text{SiH}_4$  (no HCl,  $\text{SiCl}_4=24$  sccm). Each column corresponds to a particular distance upstream from the leading edge of the epitaxial growth zone: (a) 45 mm (the most upstream location), (b) 35 mm, (c) 15 mm, (d) 13 mm, (e) 9 mm, and (f) 1 mm (the most downstream location).

further downstream compared to the  $\text{SiH}_4+\text{HCl}$  case, and can be observed closer to the growth zone (Fig. 2(f3) compared to (f2)). This is apparently due to slower  $\text{SiCl}_4$  dissociation and slower release of Si growth species compared to  $\text{SiH}_4$ .

### 3.2. Optimization of $R_g$ homogeneity

The previous experiments on low-temperature halo-carbon growth (with  $\text{CH}_3\text{Cl}$  precursor) without HCl addition relied upon a very low carrier gas flow velocity ( $\text{H}_2=1$  slm) [4]. This low carrier gas flow velocity apparently was beneficial for allowing sufficient time for gradual decomposition of Si gas-phase clusters while passing through the growth zone. Since the gas-phase nucleation of Si is entirely suppressed by using  $\text{SiCl}_4$ , the low carrier gas flow velocity is not required anymore to promote dissociation of the gas-phase clusters. Higher  $\text{H}_2$  flow rates were attempted next to improve  $R_g$  homogeneity in the  $\text{SiCl}_4$  growth (Fig. 1b).



**Fig. 3.** Linear dependence of  $R_g$  on  $\text{SiCl}_4$  flow. The absence of  $R_g$  saturation at high Si supply compared to  $\text{SiH}_4$ -based low-temperature growth [4] is consistent with eliminated consumption of Si by the homogeneous nucleation in the gas-phase.

As expected, higher  $\text{H}_2$  flows resulted in reduced precursor depletion from upstream to downstream in the hot zone. The best upstream-to-downstream homogeneity was achieved by increasing the  $\text{H}_2$  flow by a factor of 8 compared to the growth with  $\text{SiH}_4$ . Further increase of the  $\text{H}_2$  flow caused lowering of the  $R_g$  upstream due to insufficient time for  $\text{SiCl}_4$  decomposition at these too high gas flow velocities (Fig. 1b).

The use of higher  $\text{H}_2$  flow rates took away the time required for the undesirable depletion of the Si growth species by the upstream polycrystalline deposition mechanism. As a result, the amount of Si delivered to the growth zone was drastically enhanced. This in turn made the value of the effective C/Si ratio in the growth zone too low, which allowed reducing the flow of the silicon precursor to bring the effective C/Si ratio up to the appropriate value. Therefore, the  $R_g$  profiles for  $\text{H}_2=8$  and 12 slm were achieved at much lower flows of the  $\text{SiCl}_4$  precursor (1 sccm as compared to 24 sccm at  $\text{H}_2=1$  slm), for the same  $\text{CH}_3\text{Cl}$  flow rate of 6 sccm, which is equivalent to increasing the C/Si from 0.25 to 6.

### 3.3. $R_g$ dependence on the precursor flow rates and C/Si ratio

At 1300 °C and  $\text{H}_2=1$  slm, the dependence of  $R_g$  on the  $\text{SiCl}_4$  flow rate showed a normal expected increase. This was different from the  $\text{SiH}_4+\text{HCl}$  growth characterized by a weak dependence of  $R_g$  on  $\text{SiH}_4$  flow, which was caused by the polycrystalline deposition in the upstream portion of the hot zone [12]. It suggests that the effect of the upstream polycrystalline deposition



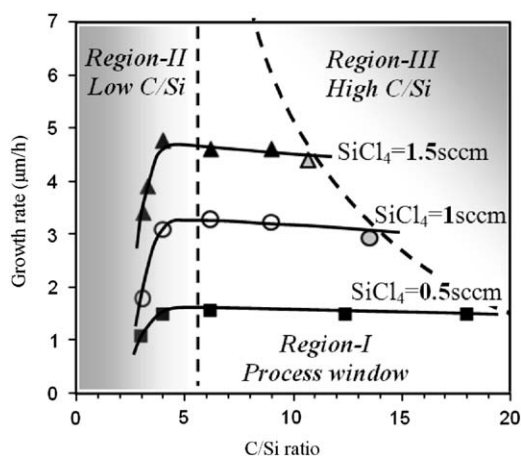
in epitaxial growth with  $\text{SiCl}_4$  is not as pronounced. Yet the polycrystalline deposition in the  $\text{SiCl}_4$  experiments caused as severe effect on  $R_g$  non-homogeneity at low carrier gas flow rate as in the  $\text{SiH}_4 + \text{HCl}$  case.

At the optimized (higher) values of  $\text{H}_2$  flow rate ( $\text{H}_2 = 8$  slm for the given reactor geometry), a normal dependence of  $R_g$  on silicon precursor flow was observed (Fig. 3).  $R_g$  increased linearly with  $\text{SiCl}_4$  flow for the entire investigated range of  $\text{Si}/\text{H}_2$  from 0 to 0.00025. The straight line of the dependence intersects the vertical axis at zero, which is an indication that there is no concurrent etching of the epilayer by  $\text{H}_2$  gas at such low growth temperatures.

There was no  $R_g$  saturation at higher values of Si precursor flow rates in contrast to the results of the low-temperature growth with  $\text{SiH}_4$  [4]. The  $R_g$  saturation in Ref. [4] was due to the increased consumption of extra Si by the homogeneous nucleation mechanism. The fact of no  $R_g$  saturation in the  $\text{SiCl}_4$ -based growth is another indication that the homogeneous nucleation in the gas phase is almost entirely eliminated by using  $\text{SiCl}_4$ .

The  $R_g$  dependence on the C/Si ratio was investigated for three different flows of  $\text{SiCl}_4$  (0.5, 1 and 1.5 sccm) by changing the  $\text{CH}_3\text{Cl}$  flow rate while keeping  $\text{SiCl}_4$  constant. The trend was qualitatively similar to the classical trend— $R_g$  increasing at low C/Si ratios and then saturating at higher C/Si ratios due to transition to the Si supply limited mode (Fig. 4).

Surprisingly, the transition from C supply limited to Si supply limited conditions took place at the value of the C/Si ratio that is much higher than one (i.e., the knee point is at  $\text{C}/\text{Si} \approx 4$  in Fig. 4). Even with the growth kinetics being significantly away from the thermodynamic equilibrium conditions, the rates of the gas-phase reactions responsible for the  $\text{CH}_3\text{Cl}$  decomposition at  $1300^\circ\text{C}$  should not be drastically different from the rate of decomposition of the Si growth precursor. The significantly higher  $\text{CH}_3\text{Cl}$  flow required for transition to the Si supply limited mode (Fig. 4) may suggest that not all C-containing products participate in surface reactions of the epitaxial growth of SiC. This could be the origin of the superiority of  $\text{CH}_3\text{Cl}$  for achieving good epilayer morphology at low growth temperatures, which is much more difficult (if not impossible) to do with more traditional hydro-carbon precursors such as propane. However, this issue is beyond the scope of this paper and will be published elsewhere.



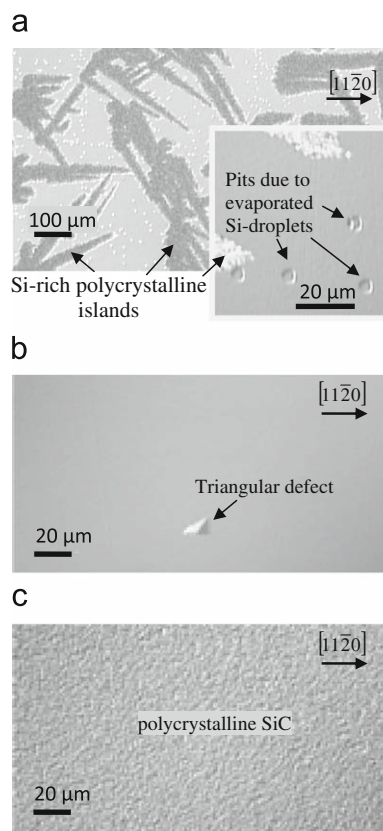
**Fig. 4.**  $R_g$  dependence on the C/Si ratio for three different  $\text{SiCl}_4$  flow rates. Regions of morphology degradation (regions II and III) correspond to low and high C/Si ratio respectively. The process window for mirror-like surface morphology (region-I) becomes narrower at higher  $R_g$ .

### 3.4. Epilayer morphology dependence on the growth conditions

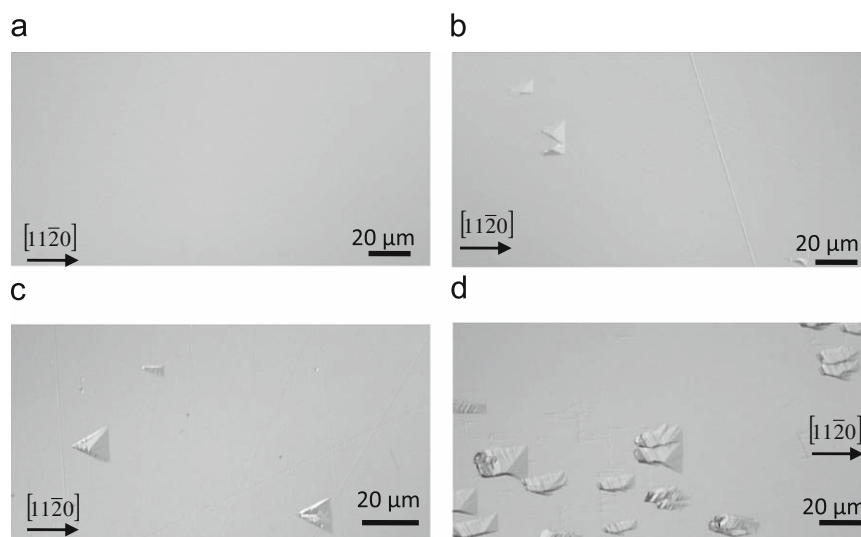
Another difference of the growth dependence on C/Si ratio at  $1300^\circ\text{C}$  from that at more traditional (i.e., higher) growth temperatures is that the entire process window providing good epilayer morphology (Region-I in Fig. 4) corresponds to the Si supply limited growth mode. For all  $\text{SiCl}_4$  flows used in this work, morphology deterioration threshold was at  $\text{C}/\text{Si} \approx 6$  (Region-II in Fig. 4). Below this critical value of the C/Si ratio, increasingly higher concentration of the triangular defects was observed (especially in the upstream portion of the growth zone). At yet lower values of C/Si ratio, the  $R_g$  reduction with the C/Si ratio was accompanied by the formation of polycrystalline Si islands (Fig. 5a) and growth pits with shape indicating that the pits' origin is related to evaporated Si droplets (the inset in Fig. 5a).

At intermediate values of the C/Si ratio (corresponding to Region-I in Fig. 4), a mirror-like epilayer morphology with rare (at least at low-to-moderate values of  $R_g$ ) triangular defects was observed (Fig. 5b). This process window for good epilayer morphology was limited on the high side of the C/Si ratio by severe morphology deterioration in the form polycrystalline SiC deposition (Fig. 5c). The grown experiments in Fig. 5 were conducted at the optimized  $\text{H}_2$  flow of 8 slm and  $\text{Si}/\text{H}_2$  of 0.000125. The values of the C/Si ratio are given in the figure caption.

It can be noted that the poly-SiC deterioration starts at the most downstream location of the epitaxial growth zone and then extends through the entire growth zone at yet higher value of the C/Si ratio. This observation, which is similar to the behavior during  $\text{CH}_3\text{Cl}/\text{SiH}_4$  low-temperature growth [4], suggests that the kinetics of  $\text{CH}_3\text{Cl}$  decomposition results in slight increase of the



**Fig. 5.** Epilayer morphology versus C/Si ratio: (a) low  $\text{C}/\text{Si} = 3.1$  resulted in Si-rich polycrystalline islands and traces of evaporated Si-droplets, (b) intermediate  $\text{C}/\text{Si} = 9$  resulted in mirror-like morphology with rare triangular defects, and (c) too high  $\text{C}/\text{Si} = 14$  caused polycrystalline SiC growth.



**Fig. 6.** Epitaxial layer morphology for four different growth rates (different  $\text{SiCl}_4$  flows). The epitaxial layers were grown at close to optimum value of C/Si ratio. For higher  $R_g$ , increasingly more triangular defects appear even at the optimized conditions. (a)  $\text{SiCl}_4=0.5$  sccm,  $R_g=1.6$   $\mu\text{m/h}$ , (b)  $\text{SiCl}_4=1$  sccm,  $R_g=3.2$   $\mu\text{m/h}$ , (c)  $\text{SiCl}_4=1.5$  sccm,  $R_g=4.8$   $\mu\text{m/h}$  and (d)  $\text{SiCl}_4=2$  sccm,  $R_g=6.4$   $\mu\text{m/h}$ .

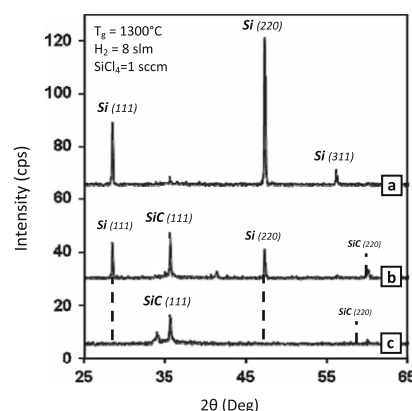
effective C/Si ratio (i.e., real C/Si ratio above the growth surface) from upstream to downstream.

While bad morphology (i.e., poly-Si islands and droplets) of Region-II (Fig. 4) starts at approximately the same value of the C/Si ratio for any  $\text{SiCl}_4$  flow (i.e., any  $R_g$ ), the deterioration at high C/Si ratio (Region-III in Fig. 4) starts at progressively lower values of the C/Si ratio when  $R_g$  (i.e.,  $\text{SiCl}_4$  flow) is increased. Apparently, the process window for good epilayer morphology (Region-I) becomes narrower at high  $R_g$ . The Region-II and Region-III eventually merge leaving no room for acceptable-quality epitaxial growth at too high  $R_g$ .

The narrowing of the process window at higher  $\text{SiCl}_4$  flow rate (i.e., higher  $R_g$ ) caused changes shown in Fig. 6, in which the surface morphology at the optimized values of the C/Si=6 sccm ratio is shown for four different growth rates. While the epilayer surface is nearly featureless at the lowest value of  $R_g=1.6$   $\mu\text{m/h}$ , progressively higher concentration of the triangular defects is observed at higher  $R_g$ . At  $R_g$  above 6  $\mu\text{m/h}$ , the triangular defects are very dense at any value of the C/Si ratio, and they merge in a nearly polycrystalline pattern at yet higher growth rates. Some other features in Fig. 6 are from the substrate as was determined by taking microscopic images of multiple locations of each substrate before the growth. The vague textures in Fig. 6(b) can be identified as underdeveloped triangles caused by less significant growth disruptions than the regular triangles. The mechanism of the triangular defect formation during the low-temperature epitaxial growth will be reported elsewhere.

The nature of the epilayer morphology deterioration at too low and too high values of the C/Si ratio (for the same values of  $\text{Si}/\text{H}_2=0.000125$ ) was investigated using powder X-ray diffraction measurements (Fig. 7) allowing identification of the chemical composition of the deteriorated disordered regions.

Naturally, the XRD set-up suitable for characterization of polycrystalline films did not detect any signals from the good quality epitaxial layers grown at the intermediate values of the C/Si ratio (Region-I in Fig. 4). The epilayer morphology deterioration at too low C/Si ratio in the form of islands (Region-II in Fig. 4) was characterized by XRD for C/Si=3.1 (corresponding to the micrograph of Fig. 5a) and for yet lower C/Si ratio equal to 1. The XRD spectra for C/Si=1 were dominated by Si lines with almost no contribution from SiC (Fig. 7 spectrum (a)). Islands produced at higher C/Si ratio of 3.1 (though still well inside the Region-II of



**Fig. 7.** XRD spectra of degraded epitaxial layers during low-temperature growth with unfavorable values of C/Si ratio: (a) C/Si=1, (b) C/Si=3.1 (both corresponding to Region-II of Fig. 4) and (c) C/Si=14 (corresponding to Region-III of Fig. 4). Morphology degradation at low C/Si ratio ((a) and (b)) involves formation of Si-rich polycrystalline phase. Too high C/Si ratio causes purely SiC polycrystalline degradation (c).

Fig. 4) still showed strong Si-related XRD lines, as well as contribution from polycrystalline 3C-SiC (Fig. 7 spectrum (b)).

The morphology deterioration at too high C/Si ratio (Region-III in Fig. 4 and the micrograph of Fig. 5c) showed only SiC without Si-related XRD lines (Fig. 7 spectrum (c)). XRD confirmed that too high C/Si ratio causes epilayer degradation in the formation of polycrystalline 3C-SiC films.

### 3.5. Discussion of the growth rate and morphology trends

The value of  $R_g$  was increased in the low-temperature epitaxial growth experiments with  $\text{SiCl}_4$  replacing  $\text{SiH}_4+\text{HCl}$  for the same flow rate of the Si precursor (Fig. 1a). This confirmed that  $\text{SiCl}_4$  is even more efficient in suppressing the homogeneous nucleation. However, the  $R_g$  non-homogeneity and the enhanced generation of the triangular defects indicated that slower dissociation of  $\text{SiCl}_4$  does not eliminate the problem of premature (or even excessive) supply of Si growth species to the surfaces of the hot zone and the substrate.

It was relatively easy to address the problem of the excessive supply of Si at the upstream portion of the hot zone by increasing

the carrier gas flow velocity and thus reducing the residence time. This improved  $R_g$  homogeneity (Fig. 1b) and simultaneously reduced consumption of the Si growth precursor. It should be noted that such straightforward recipe of using high  $H_2$  flow rates was impossible in the low-temperature growth with  $SiH_4$  precursor, which relied upon quick formation of Si gas-phase clusters and their subsequent gradual dissociation in the growth zone enabled by the sufficient residence time at low  $H_2$  flow rates [4].

It is more difficult to address the problem of morphology degradation (and formation of the triangular defects in particular) at high  $R_g$  (Fig. 6). The effect of too high C/Si ratio (Fig. 5c) is apparently similar to the morphology degradation in  $CH_3Cl/SiH_4$  growth [4]. The formation of polycrystalline SiC can be avoided by reducing the C/Si ratio, for example by increasing the flow of the Si precursor.

In the low-temperature growth with  $SiH_4$  [4], an increase of both Si and C precursor flows resulted in an increase of the C/Si ratio due to consumption of all of the extra Si by gas-phase clusters. Therefore, an attempt to increase  $R_g$  beyond a certain point unavoidably caused increase of the effective C/Si ratio. In contrast to the growth with  $SiH_4$ , the absence of Si nucleation in the gas phase during the growth with  $SiCl_4$  allows reducing the effective C/Si ratio by simply increasing the  $SiCl_4$  flow rate. Consequently, the main problem of the low-temperature growth with  $SiH_4$  – inability to increase  $R_g$  without causing unintentional increase of the effective C/Si ratio – seems to be eliminated.

However, this expected improvement introduced a new problem. While all the “excessive” Si was automatically converted into Si gas-phase clusters during the low-temperature growth with  $SiH_4$ , in the  $SiCl_4$  growth the unrestricted availability of extra Si for surface reactions brings its own disadvantages. At such low growth temperatures (well below the melting point of Si), an excess of Si may be as important source of morphology degradation as an excess of C. At the extreme, the excessively low C/Si ratio (i.e., excessive supply of Si over C) leads to the formation of Si droplets (or growth pits due to briefly formed and then evaporated droplets) and even Si-rich polycrystalline islands (Fig. 5a).

An obvious recipe would be to stay sufficiently far away from both Region-II and Region-III in Fig. 4. However, as follows from Fig. 4, the boundary of the too high C/Si ratio (Region-III) moves to lower values of the C/Si ratio at higher  $R_g$ . This means narrowing and eventually disappearance of the process window (Region-I).

As was noted above, the transition to the Si supply-limited mode occurs at the value of the input C/Si ratio much higher than one (Fig. 4). This possibly reveals additional advantages of using  $CH_3Cl$  (with any Si precursor) for homoepitaxial growth of SiC at low temperatures as compared to more traditional hydro-carbon precursors. It might be suggested that significantly different C-related species arrive to the growth surface when a halo-carbon precursor is used. With possibly lower surface reactivity of the C-related products of  $CH_3Cl$  decomposition, a susceptibility to 2-dimensional and 3-dimensional nucleation might be reduced in favor of the desirable step-flow growth or species desorption from the surface. While reducing the effective C supply for various surface reactions, this also favors better epilayer morphology.

#### 4. Conclusion

Similar to the experience with chloro-silane precursors used in high-temperature epitaxial growth of SiC [7–9], use of  $SiCl_4$  for

low-temperature epitaxial growth (growth at 1300 °C) was proven to be the most efficient for nearly complete elimination of the homogeneous nucleation of Si in the gas phase. This made it possible to avoid unintentional increase of the effective C/Si ratio when attempting increase of the growth rate, which was considered to be the main bottleneck of the low-temperature growth with  $SiH_4$ .

However, a possibility to provide an excess of Si supply to the growth surface revealed a new bottleneck for achieving high values of  $R_g$  without morphology degradation. At such low temperatures, any significant excess Si over C resulted in appearance of Si droplets at the surface as well as nucleation of Si-rich islands, which was prevented from happening by the homogeneous nucleation in  $SiH_4$ -based growth.

On the other hand, staying sufficiently far away from the dangerously low C/Si ratio becomes increasingly difficult when  $R_g$  is increased. At higher  $R_g$ , the region of morphology degradation caused by excessive supply of carbon shifts to lower values of C/Si ratio. At growth rates above 5–6  $\mu m/h$ , the process window for the good-quality low-temperature growth becomes too narrow, which causes high concentration of triangular defects at any value of C/Si ratio and eventually polycrystalline deposition.

Apparently, a possibility to control undesirable Si nucleation at the epilayer surface at low C/Si ratios should be evaluated by altering other process conditions such as the growth pressure, additional supply of chlorine-containing species capable of suppressing undesirable surface reactions, use of different chloro-carbon precursors having higher Cl/C ratio, etc. These efforts are beyond the scope of this paper and will be reported elsewhere.

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