I. INTRODUCTION

Modern silicon carbide (SiC) homoepitaxial growth techniques for high power, high frequency, high temperature, and high radiation-resistant electronics strive to improve the crystalline quality and purity and achieve increasingly higher growth rates. The hot-wall chemical vapor deposition (CVD) growth concept\(^1\) was an important breakthrough development enabling low gradient of temperature in the growth zone, enhanced precursor cracking efficiency, improved control of the homogeneous gas-phase nucleation of Si, and other advantages.

Development of the so-called high-temperature chemical vapor deposition (HTCVD) using the hot-wall reactor concept revealed a critical role of the homogeneous gas-phase nucleation and Si clusters formation in the gas phase.\(^2\) Suppressed formation (or timely dissociation) of Si clusters is considered crucial for avoiding undesirable depletion of the growth precursors caused by trapping of Si growth species in low-diffusivity clusters in the gas phase. The cluster dissociation mechanism is also important for controlling the effective silicon-to-carbon (Si/C) ratio above the growth surface and for preventing morphology degradation caused by raining of Si clusters (droplets) onto the growth surface.

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Development and investigation of the halo-carbon low-temperature epitaxial growth technique\(^3\) revealed that Si vapor condensation may be even more crucial at low growth temperatures \((T_g)\). While device-quality epitaxial layers were demonstrated at temperatures below 1300 °C using chloromethane \((\text{CH}_3\text{Cl})\) as a halo-carbon precursor in place of the traditional precursor propane, it was difficult to achieve growth rates above \(2–3 \text{ mm/h} \) without morphology degradation.\(^4\) It was demonstrated that the Si homogeneous gas-phase nucleation mechanism is responsible for saturation of the supply of Si species to the growth surface when the flow rates of SiH\(_4\) are increased beyond a certain value. The growth rate \((R_g)\) became independent of the silane flow rate beyond a certain threshold of the SiH\(_4\) flow. Attempts were made to increase \(R_g\) beyond \(2–3 \text{ mm/h} \) by increasing the flow rates of SiH\(_4\) and CH\(_3\)Cl. However, the Si homogeneous gas-phase nucleation made the effective Si/C ratio very much lower than the input Si/C ratio, thereby shifting the operating point away from the process window compatible with the desirable step-flow growth.

It can be concluded that while the delivery of chlorine by the CH\(_3\)Cl precursor is important for our ability to grow SiC at such low temperatures,\(^4\) the amount of chlorine is not sufficient to suppress the homogeneous nucleation of Si in the gas phase. An additional supply of chlorine should be attempted to further suppress Si condensation.
A possibility of improving $R_g$ and the morphology of the regular-temperature homoepitaxial growth of SiC (i.e., $T_g$ above 1500 °C) by adding chlorinated gases during the growth has long been investigated. Initially, HCl-based experiments were focused on the surface-reaction mechanisms. An enhancement of the surface migration of adatoms caused by HCl-assisted suppression of two-dimensional nucleation was demonstrated. Later, multiple groups successfully employed addition of HCl during the regular-temperature epitaxial growth for addressing the Si vapor condensation problems. A possibility of increasing the growth rate without morphology degradation was demonstrated. The improvements were attributed to suppressed gas-phase homogeneous nucleation, which results in enhanced supply of Si species to the growth surface. Subsequently, qualitatively similar improvements caused by the use of chlorinated silicon precursors (e.g., trichlorosilane and methyltrichlorosilane) supported the model of the suppressed Si vapor condensation. The role of different chlorinated species was evaluated using classical nucleation theory and quantum mechanical refinement. Theoretical calculations suggested that the gas-phase chemistry should be significantly influenced by the addition of chlorine-containing species.

The potential benefits of having more chlorine in the growth zone of the reactor were also explored in the low-temperature epitaxial growth of SiC. The HCl addition during the halo-carbon growth at 1300 °C was successful for: (1) improving the growth rate for otherwise same growth conditions and (2) making it possible to additionally enhance the growth rate without morphology degradation by increasing the precursor flow rates.

However, in spite of all the efforts to provide evidence supporting the mechanism of HCl-induced gas-phase cluster dissociation (or suppressed homogeneous nucleation) during the regular-temperature growth (i.e., $T_g$ above 1500 °C), as well as during the low-temperature epitaxial growth (i.e., $T_g$ down to 1300 °C and below), the available experimental pieces of evidences are limited to the observations of the increased $R_g$ and improved epilayer quality. Therefore we have little support for the gas-phase cluster dissociation mechanism and no sufficient understanding required for using the HCl addition with the maximum efficiency. The incompleteness of our knowledge about the HCl effect is particularly obvious for the low-temperature epitaxial growth. The trends reported in Ref. 12 for 1300 °C growth with HCl were rather complicated and did not allow attributing the improvements merely to the increase in the Si supply to the growth surface caused by HCl-induced dissociation or suppressed formation of the Si gas-phase clusters.

This paper provides more direct experimental evidence for the influence of chlorine-containing species on the gas-phase reactions during the low-temperature homoepitaxial growth. It also reveals some undesirable side effects of the premature Si cluster dissociation.

II. EXPERIMENTAL PROCEDURE

Low-temperature epitaxial growth experiments were conducted in a hot-wall CVD reactor at 100–200 Torr with H$_2$ as the carrier gas and SiH$_4$ (3% in H$_2$) as the silicon source. The design of the reactor was similar to the common design of the hot-wall reactors used by the majority of the research groups for the regular-temperature (i.e., $T_g$ above 1500 °C) growth. No modifications to the design were introduced for the low-temperature growth. CH$_3$Cl was used as the carbon source in place of the traditional propane. A typical growth experiment utilized 10×10 mm$^2$ square pieces of standard commercially available n-type 4H-SiC substrates. Substrates were vicinally cut 8° toward the [11−20] direction. A few pieces of the substrate were placed at different locations of the susceptor on the top of a 2-in.-diameter carrier wafer, which ensured that the thermal conditions are equivalent to the growth on a full-wafer substrate.

In addition to 10×10 mm$^2$ pieces, full 2-in.-diameter wafer growth experiments were also successfully conducted at 1300 °C. Different flow rates of HCl gas from 0 to 25 SCCM (SCCM denotes cubic centimeter per minute at STP) were used in different growth experiments.

The epilayer thickness maps were obtained by reflective Fourier transform infrared spectroscopy. Surface morphology was examined by Nomarski optical microscopy. Capacitance-voltage (C-V) measurements were used to characterize unintentional doping. A Rigaku Ultima III 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.

III. RESULTS

In order to achieve higher growth rates at $T_g$ as low as 1300 °C, relatively high flow rates of silicon precursor SiH$_4$ in combination with relatively low H$_2$ carrier gas flow rates (with the particular values depending also on the reactor geometry) were used in the previous work on low-temperature halo-carbon growth. Even higher SiH$_4$ flow rates (more than 30 SCCM) were occasionally employed in this paper in order to make the effect of Si vapor condensation easier to detect.

A cloud of Si gas-phase clusters was routinely observed inside the hot-wall susceptor during the low-temperature growth, and the cloud became increasingly denser with increasing SiH$_4$ flow rate. The dense cluster cloud shown in Fig. 1(a) was photographed though the rear port of the reactor during the growth at a very high SiH$_4$ flow rate of 20 SCCM.

The observation of the reduced density in the Si cluster cloud with addition of HCl served as the first evidence of enhanced Si gas-phase cluster dissociation (or suppressed nucleation) caused by HCl. The cloud became visibly less dense at HCl flow rates as low as a few standard cubic centimeters per minute. At the HCl flow rate of 20 SCCM, only a faint cloud was observed inside the susceptor [Fig. 1(b)].

Unfortunately, the reactor design did not offer a practical possibility to establish how far upstream from the leading edge of the susceptor the Si cluster cloud starts forming, how far it extends inside the susceptor before a significant (if any) thermal dissociation of the Si gas-phase clusters takes place, and, the most important, what part of the cluster cloud distribution along the gas flow direction is predominantly at-
tacked by the added HCl. Therefore relevant growth dependencies helping to answer some of these questions are discussed below.

A. The growth rate and the effective Si/C ratio versus the HCl flow rate

The most important anticipated outcome of the HCl addition is the increase in the growth rate ($R_g$). A significant increase in $R_g$ was indeed observed under certain HCl flow rates at some (but not all) growth conditions. However, the $R_g$ dependence on the HCl flow rate was far from being straightforward (Fig. 2). This experiment was conducted with SiH$_4$ flow rate of 24 SCCM and CH$_3$Cl flow rate of 4 SCCM; however growth with SiH$_4$ flow down to at least 8 SCCM produced qualitatively similar trends.

The low-temperature halo-carbon growth without HCl is characterized by a very good $R_g$ homogeneity along the gas flow direction (the bottom $R_g$ profile in Fig. 2). The addition of HCl at 2 SCCM caused more than 40% increase in $R_g$ for the particular growth conditions while preserving the good $R_g$ homogeneity (Fig. 2).

The HCl flow rate of 5 SCCM caused further increase in $R_g$ upstream of the growth zone exceeding 70% in comparison to the no-HCl growth (Fig. 2). However, $R_g$ at the center of the growth zone increased much less. At the downstream portion of the growth zone, $R_g$ with the HCl flow rate of 5 SCCM was actually lower than that with the lower HCl flow rate of 2 SCCM.

Quite unexpected results were observed at HCl flow rate of 8 SCCM. $R_g$ decreased everywhere compared to the case with the HCl flow rate of 5 SCCM, while the nonhomogeneity of the $R_g$ profile (i.e., the decrease in $R_g$ from upstream to downstream) remained qualitatively similar (Fig. 2). It should be noted that a qualitatively similar strange reduction in $R_g$ was clearly observed at the variety of growth conditions.

Further increase in the HCl flow rate resumed the trend of $R_g$ increase with increasing HCl supply. However, the change was much less significant than that at lower HCl flow rates, showing the trend of saturating at higher HCl flows. The two main observations from this trend are: (1) a complex nonmonotonous change in $R_g$ upstream of the growth zone should leave less species available for the growth downstream. However, our computational fluid dynamics (CFD) simulations indicated that the magnitude of such depletion mechanism is not sufficient to cause the $R_g$ nonhomogeneity even remotely close to the one shown in Fig. 2. Another precursor depletion mechanism is required to explain this outcome.

The trend of $R_g$ dependence on the HCl flow rate discussed above is plotted in Fig. 3 for a selected location close to the middle of the growth zone. In general, an increase (or a decrease) in $R_g$ can be caused by an increase (or decrease) in Si supply to the growth surface, by an increase (or decrease) in carbon supply, or both. If the changes in the supply of Si and carbon are not proportional, this may lead to changes in the effective Si/C ratio above the growth surface. When considering the anticipated effect of the HCl addition with the other growth conditions kept the same, we expect the increase in both $R_g$ and the effective Si/C ratio due to enhanced supply of Si species released from the Si gas-phase clusters. It is possible to qualitatively monitor the changes in the effective Si/C ratio by observing the changes in doping caused by the site competition mechanism$^{13}$ as long as we account for other possible influences, such as doping increase that happens with increasing $R_g$ at constant effective Si/C ratio.$^{14}$

![FIG. 1. Rear view of the heated susceptor and the cloud of the silicon gas-phase clusters inside the susceptor during 1300 °C epitaxial growth: (a) without HCl and (b) with 10 SCCM of HCl added. Suppressed cluster formation caused by Cl-related products is evidenced by the drastically reduced density in the cluster cloud in (b).](image)

![FIG. 2. Growth rate ($R_g$) as a function of the distance from the leading edge of the susceptor for different values of HCl flow rates compared to the growth without HCl. Notice the $R_g$ reduction at 8 SCCM compared to 5 SCCM.](image)
In order to trace the changes in the effective Si/C ratio accompanying the changes in $R_g$ caused by HCl addition, the net donor concentration measured by the C-V technique is also plotted versus the HCl flow rate in Fig. 3. It is obvious that the changes in the effective Si/C ratio do not follow the simple trend expected from enhanced release of Si species due to HCl. From 5 to 8 SCCM of HCl flow, the increase in $R_g$ with increasing the HCl flow rate below 3 SCCM would cause an increase (rather than decrease) in the doping if the effective Si/C ratio remained constant.

Concerning the second alternative possibility, the dependence of doping on $R_g$ at a constant Si/C ratio without HCl was determined in Ref. 14 and is shown in the inset of Fig. 3. It is clear that the doping dependence on $R_g$ could only mask the total doping dependence on HCl, but it cannot be the cause for the observed doping trend. For example, the decrease in $R_g$ with increasing the HCl flow rate below 3 SCCM would cause an increase (rather than decrease) in the doping if the effective Si/C ratio remained constant.

This confirms that the HCl addition indeed caused a decrease in the effective Si/C ratio (or more precisely an increase in the C/Si ratio) in this small HCl flow range, possibly due to more significant supply of carbon growth species than the supply of silicon species. However, the conventional model for the HCl effect suggests that the only outcome of the HCl addition should be the release of Si species from the gas-phase clusters and an enhanced supply of those species to the growth surface. It would be unclear within the framework of the conventional model for the HCl effect why the carbon supply is enhanced during the HCl-assisted dissociation of the Si gas-phase clusters in this low range of the HCl flow rates. Consequently, carbon involvement in the gas-phase homogeneous nucleation process should be considered.

The drop in $R_g$ at HCl flow rates above 5 SCCM, which is accompanied by continuation of the increase in the net donor concentration, also confirms that it is the change in the effective Si/C ratio that is responsible for the change in doping. In this range of the HCl flow rates, the $R_g$ reduction with HCl is probably the result of a reduction in the carbon supply. However, it would be unclear within the framework of the conventional model for the HCl effect why the carbon supply to the growth surface is reduced in this intermediate range of the HCl flow rate.

One should be careful when judging the changes in the effective Si/C ratio by looking only at the doping trend. However, an additional confirmation can be gained from observing the epilayer surface morphology. Numerous prior experiments with and without HCl addition provided consistent information about how exactly the surface morphology degrades when the Si/C ratio is reduced. The changes in the epilayer morphology for different values of the HCl flow rates (Fig. 4) support the conclusion about the changes in the effective Si/C ratio caused by HCl addition. The morphology is characteristically degraded at HCl flow of 2 SCCM [Fig. 4(b)] in comparison to the no-HCl growth [Fig. 4(a)]. By itself, this degradation could be attributed to the increase in $R_g$, which indeed takes place for this HCl flow rate (Fig. 3).
However, the next HCl flow rate of 5 SCCM shows a clear improvement of the epilayer surface morphology [Fig. 4(c)], even though \( R_g \) becomes even higher. Therefore, the changes in \( R_g \) caused by the HCl flows of 2 and 5 SCCM confirm our prior conclusion about the reduction and the increase in the effective Si/C ratio, respectively. The epilayer morphology at higher HCl flows [including the flow of 22 SCCM shown in Fig. 4(d)] is nearly featureless, which is also consistent with the higher values of the effective Si/C ratio.

Finally, one should note that there is neither a direct nor reverse correlation between \( R_g \) and the effective Si/C ratio in Fig. 3 when the HCl flow is increased. The only conclusion that can be made at this point is that the release of Si from the gas-phase clusters and the resulting enhanced supply of Si species to the growth surface are not the only outcomes of the HCl addition. The HCl addition seems to change (and not always increase) the supply of both silicon and carbon species to the growth surface, and those changes may be different for carbon and silicon depending on the actual HCl flow rate. A more detailed model explaining this complex behavior is suggested below.

### B. The growth rate dependence on the precursor flow rates

A complex dependence of \( R_g \) on the SiH\(_4\) flow rates in the absence of HCl was established in the previous work.\(^4\) The dependence was influenced by the homogeneous gas-phase nucleation and the resulting saturation of Si supply to the growth surface at high SiH\(_4\) flows. It was expected that the addition of HCl would eliminate this kind of saturation and lead to higher growth rates when SiH\(_4\) flow is increased (at least until the growth becomes carbon limited, which is not the case until very high SiH\(_4\) supply\(^4\)). The effect of the HCl addition on \( R_g \) was expected to be more pronounced for higher than for lower SiH\(_4\) flow rates.

In reality, the precursor flow dependencies for HCl-assisted growth turned out to be much different from the expectations. The \( R_g \) dependence on CH\(_3\)Cl flow was normal when HCl was added (i.e., an increase in \( R_g \) with the CH\(_3\)Cl flow rate). However, the dependence on SiH\(_4\) flow became even more complicated with the HCl addition. In a wide range of SiH\(_4\) flows from below 4 to above 30 SCCM, \( R_g \) showed a weak dependence on the silane flow. Moreover, in this weak dependence, \( R_g \) would actually slightly increase with decreasing the SiH\(_4\) flow rate.

In combination with the observation of deteriorated \( R_g \) homogeneity from upstream to downstream discussed above, the trend of weak SiH\(_4\) flow dependence supports the possibility of an additional mechanism of the growth species depletion in the presence of HCl, which competes with the desirable release of silicon from the gas-phase clusters. Therefore, the dependencies were also investigated at higher H\(_2\) carrier gas flow rates to evaluate the “earlier” stages of the gas phase kinetics.

At H\(_2\) flow of 2.5 l/min during the growth with HCl addition, the \( R_g \) homogeneity upstream-to-downstream somewhat improved, thus supporting the hypothesis of precursor depletion (Fig. 5). The \( R_g \) dependence on the CH\(_3\)Cl flow rate remained normal—\( R_g \) was increasing with increasing CH\(_3\)Cl flow [Fig. 5(a)]. The \( R_g \) dependence on the SiH\(_4\) flow remained weak [Fig. 5(b)]. While \( R_g \) in the upstream portion of the growth zone did show a slight (~5%) increase when the SiH\(_4\) flow rate changed from 9 to 24 SCCM, the downstream regions showed a reverse correlation (lower \( R_g \) at higher SiH\(_4\) flows), which is qualitatively similar to the growth with lower H\(_2\) flow rates.

This trend further supports the possibility of a previously unaccounted mechanism of precursor depletion in the presence of HCl, which predominantly affects the downstream regions, especially at low carrier gas flow rates. In order to confirm that the carbon species also get significantly depleted along with Si, the distribution of the net donor concentration from upstream to downstream was examined. The net donor concentration (and consequently the Si/C ratio) somewhat increased from upstream to downstream, even though \( R_g \) was reduced downstream (Fig. 6). Simultaneously, while the doping increased everywhere with increasing the SiH\(_4\) flow rate, this change was relatively small (Fig. 6).

From the following observations—(1) \( R_g \) decreases from upstream to downstream, (2) \( R_g \) also decreases (at least in the downstream regions) with increasing the SiH\(_4\) flow, and (3) the effective Si/C ratio does not change much or slightly increases with increasing the SiH\(_4\) flow—it can be concluded that not only depletion of Si but also a significant (and sometimes dominating) depletion of carbon species must be taking place in the presence of HCl.

### C. HCl-enhanced polycrystalline deposition

It was further established that higher carrier gas flow rates are not practical for improving the HCl-induced \( R_g \).
nonhomogeneity from upstream to downstream. Severe morphology degradation in the form of polycrystalline islands appeared in the upstream portion of the growth zone [i.e., the substrate area] at higher H2 flow rates of 2.5 l/m [Fig. 7(a)]. The island size and concentration reduced from upstream to downstream. Also, the average size of the islands observed on the substrate was proportional to the HCl flow rate while being insignificant in the growth experiments without HCl [Fig. 7(b)].

The HCl effect on the formation of polycrystalline islands was further investigated in the upstream portion of the hot zone. A few pieces of SiC substrates were placed in the upstream region of the susceptor at different distances upstream from the growth zone, as well as on the protruding portion of the thermal insulation foam upstream from the susceptor. The surface morphology for no-HCl growth is shown in Figs. 8(a)–8(e) and that for the growth with HCl flow rate of 22 SCCM is shown in Figs. 8(f)–8(j). The two leftmost micrographs in Fig. 8 [i.e., micrographs (a) and (f)] correspond to the most upstream samples. Each micrograph in Fig. 8 has a corresponding number in millimeters, indicating the distance from the leading edge of the susceptor (positive numbers for the samples placed on the susceptor and negative numbers for the samples placed on the thermal insulation foam upstream from the susceptor).

No epitaxial growth and polycrystalline deposition were observed until approximately −20 mm upstream from the leading edge of the susceptor for the particular gas flow ve-

FIG. 6. The net donor concentration at higher carrier gas flow velocity as a function of the distance from the leading edge of the growth zone for different values of SiH4 flow rates. The growth rate profile for the SiH4 flow of 24 SCCM from Fig. 5(b) is also shown for comparison. The HCl flow rate used was 22 SCCM.
SiH$_4$ flow rates used in this work, a vigorous formation of polycrystalline deposits took place upstream from the susceptor, (c) and (h) inside the susceptor at 10 mm from its upstream edge, (d) and (i) inside the susceptor at 12 mm from its upstream edge, and (e) and (j) inside the susceptor at 20 mm from its upstream edge (which is 5 mm from the substrate).

FIG. 8. Optical micrographs of the polycrystalline deposits on pieces of SiC wafers placed in the upstream regions of the hot zone: the top—no HCl, and the bottom—with HCl=22 SCCM. The location of (a) and (f) was 20 mm upstream from the susceptor, (b) and (g) at 10 mm upstream from the susceptor, (c) and (h) inside the susceptor at 10 mm from its upstream edge, (d) and (i) inside the susceptor at 12 mm from its upstream edge, and (e) and (j) inside the susceptor at 20 mm from its upstream edge.

FIG. 9. XRD spectra of the polycrystalline deposits after epitaxial growth without HCl at different locations of the hot zone along the gas flow direction: (a) more upstream location corresponding to Fig. 8(b) and (b) more downstream location corresponding to Fig. 8(c). The spectra are shifted in the vertical direction for clarity. Spectrum (a) is scaled down 0.4 times.

Only two more millimeters downstream, the islands become very rare [Fig. 8(d)]. At the distance of 20 mm from the leading edge of the susceptor (which is only 5 mm to the leading edge of the growth zone), no polycrystalline deposits were observed in the experiments without HCl. Instead, a regular epitaxial growth but with deteriorated morphology took place [Fig. 8(e)].

The most pronounced differences caused by the high HCl flow rate can be observed starting with the sample placed 10 mm downstream from the susceptor leading edge [Fig. 8(h)]. There is no reduction in the polycrystalline deposits in this region compared to the more upstream locations. Actually, the polycrystalline deposition appears to be somewhat more significant according to XRD results.

At high HCl flow, the rate of polycrystalline deposition starts gradually decreasing toward downstream when approaching the growth zone, but this transition is much slower than in the experiments without HCl. The sample placed at 12 mm downstream from the susceptor leading edge [Fig. 8(i)] shows almost strong deposits as the more upstream sample [Fig. 8(h)], with only rare spaces between the polycrystalline islands.

Even at the location of 20 mm downstream from the leading edge of the susceptor (5 mm to the leading edge of the growth zone), relatively big islands of polycrystalline deposits were observed [Fig. 8(j)]. This is in contrast to the complete absence of the polycrystalline deposits at the same location in the growth without HCl [Fig. 8(e)]. In addition, the morphology of the epitaxial growth in the regions of this location that are free from polycrystalline deposits is much better in the growth with HCl than that without HCl, which serves as evidence of the higher effective Si/C ratio in this region when HCl is used.
It is more logical to suggest that the boundaries of the region of the polycrystalline deposition along the gas flow direction are determined by the gas-phase reaction kinetics. The early-stage products of SiH$_4$ decomposition and/or very high concentrations of species delivered to the wall surfaces are responsible for the polycrystalline deposition when the supply of SiH$_4$ is sufficiently high [e.g., Figs. 8(b) and 8(g)]. Quick reduction in the polycrystalline deposition further downstream in the growth without HCl [Figs. 8(c) and 8(d)] can be explained by the well known mechanism of the Si gas-phase homogeneous nucleation. The consumption of Si-containing products of SiH$_4$ decomposition by the Si clusters in the gas phase makes this Si unavailable for the polycrystalline deposition. The Si gas-phase clusters are known to have lower diffusivity in the gas phase, which prevents them from reaching the surface of the thermal insulation foam or the susceptor and deposit there. Consequently, further downstream there is not enough Si to form any polycrystalline phases [Fig. 8(e)].

Simultaneously, at these locations, the temperature is high enough to cause a significant decomposition of the carbon precursor CH$_3$Cl. The depletion of Si by the gas-phase clustering process and simultaneous significant supply of carbon results in a low value of the effective Si/C ratio, which explains the epilayer morphology deterioration in Fig. 8(e) in accordance with the trend reported in Ref. 4. Deeper inside the susceptor (i.e., in the growth zone), higher temperatures are known to enhance dissociation of the Si gas-phase clusters, thus increasing the effective Si/C ratio and enabling good epilayer quality. However, as was previously established, a significant amount of clusters remain not dissociated, thus keeping Si away from the epitaxial growth and limiting $R_g$.

The changes caused by the addition of HCl are consistent with the model proposed above. The formation of Cl-containing intermediate Si products in the gas phase or HCl-induced etching/dissociation of newly formed Si gas-phase clusters in the upstream portion of the hot zone prevents or significantly reduces the Si consumption and depletion by the clustering mechanism. However, this HCl-enhanced availability of Si species also causes much higher polycrystalline deposition in the upstream portion of the hot zone than during the growth without HCl [Figs. 8(h)–8(j) versus Figs. 8(c)–8(e)].

Also, considering the epitaxial component of the surface reactions at the location that is closer to the growth zone [Figs. 8(e) and 8(j)], the reduced depletion in Si species by the gas-phase clustering mechanism in the presence of HCl ensures a higher value of the effective Si/C ratio, which could explain the improved epilayer morphology in Fig. 8(j) (except for the rare polycrystalline islands) compared to Fig. 8(e). It follows from Fig. 10 that in the growth with HCl, an additional region in the upstream portion of the hot zone (from $\sim$45 mm to more than 65 mm) participates in the polycrystalline deposition, while no deposition takes place in this region without HCl. This additional polycrystalline deposition enabled by HCl serves as an additional mechanism for both precursors’ depletion.

The addition of HCl also causes a desirable postponed dissociation of those gas-phase clusters that managed to form in spite of the HCl effect and reached the growth zone of the reactor. This explains the $R_g$ increase with addition of HCl (Fig. 2). Simultaneously, the new mechanism of precursor
depletion by polycrystalline deposition can explain why \( R_g \) increases less than expected and also why \( R_g \) reduces from upstream to downstream in the growth zone. While the quantitative model is yet to be developed, this new mechanism of depletion could also be responsible for the complex dependence of \( R_g \) on the HCl flow rate (Fig. 3). At some HCl flow rates, the depletion of the growth species caused by polycrystalline deposition outweighs the HCl-induced enhancement of the Si supply caused by the gas-phase cluster dissociation in the growth zone, which results in \( R_g \) reduction with HCl flow.

The polycrystalline deposition in more upstream regions of the hot zone only depletes Si, since the carbon precursor CH\(_3\)Cl is not yet dissociated. However, the precursor depletion by polycrystalline deposition in the regions closer to the growth zone also involves carbon species, which is evidenced by XRD revealing the presence of carbon in the polycrystalline deposits. Obviously, silicon and carbon gas-phase species are not depleted equally, and their relative depletion appears to depend on the HCl flow rate. This could explain, at least partially, the complex dependence of the effective Si/C ratio (i.e., net donor concentration) on the HCl flow rate (Fig. 3).

On the other hand, the reduction in the effective Si/C ratio accompanying the increase in \( R_g \) at low HCl flow rates up to 3 SCCM in Fig. 3 calls for a hypothesis that carbon is also involved in the gas-phase clusters, which is independent of the polycrystalline deposition mechanism. Possible HCl-induced release of carbon from such clusters outpacing the release of Si would explain the increase in \( R_g \) and the reduction in the Si/C ratio at low HCl flows. Since the carbon precursor CH\(_3\)Cl dissociates slower (i.e., more downstream) than SiH\(_4\) (Fig. 10), the carbon may incorporate in the gas-phase clusters only after the silicon core of the clusters had been formed. This would explain the HCl-induced release of carbon from such clusters outpacing the release of Si at low HCl flows (e.g., when the amount of HCl added is small and only sufficient to etch the carbon-rich top layers of the clusters). The involvement of carbon in the gas-phase clusters (i.e., formation of Si–Si\(_{C1−x}\) clusters) was suggested in the HTCVD epitaxial growth of SiC.\(^{15,16}\) In the current work, it is suggested for the first time that the Si homogeneous gas-phase nucleation during epitaxial growth at low temperatures forms gas-phase clusters that can also capture carbon.

The combination of the mechanisms suggested above explains the complex dependence of \( R_g \) and the effective Si/C ratio on the HCl flow rate observed in Fig. 3. This complex influence can be summarized as follows.

- The first region of the dependence (low HCl flow rates below 2 SCCM in Fig. 3): The amount of HCl is only sufficient to etch the very top carbon-rich layers of gas-phase clusters. The supply of carbon species from the clusters exceeds the supply of silicon species. This causes increase in \( R_g \) and reduction in the effective Si/C ratio. Simultaneously, the polycrystalline deposits are formed mostly upstream of the hot zone; only silicon but no carbon is involved in those deposits.
- The second region of the dependences (low-to-intermediate HCl flow rates from 2 to 5 SCCM in Fig. 3): The polycrystalline deposits are still formed mostly upstream of the hot zone. In those regions, the carbon source CH\(_3\)Cl is not dissociated yet; therefore only silicon but no carbon gets consumed by those deposits. The amount of HCl is sufficient to etch the gas-phase clusters much more significantly. After the top carbon-rich layers of the clusters are removed, the release of silicon dominates. This causes an increase in both \( R_g \) and the effective Si/C ratio.
- The third region of the dependence (intermediate HCl flow rates from 5 to approximately 8 SCCM in Fig. 3): The enhanced etching of the gas-phase clusters releases more Si and causes formation of polycrystalline deposits closer to the growth zone (i.e., at the locations where, in the experiments without HCl, vigorous gas-phase clustering of silicon kept Si species away from forming those deposits). At these locations, a significant fraction of CH\(_3\)Cl is already dissociated. The carbon gets depleted by its trapping in polycrystalline deposits. This causes the sharp reduction in \( R_g \) and increase in the Si/C ratio (Fig. 3).
- The last region of the dependence (high HCl flow rates above 10 SCCM in Fig. 3): Essentially all gas phase clusters are dissociated. Further increase in HCl does not cause any sharp effects. The moderate increase in \( R_g \) and decrease in the Si/C ratio could imply a moderate supply of carbon not related to cluster dissociation or island formation mechanism (e.g., influence of HCl on the surface kinetics of the epitaxial growth and moderate etching of the graphite insulation foam).

The effect of HCl on the pattern of the polycrystalline deposits can also explain the \( R_g \) dependence on the precursor flow rates (Fig. 5). While carbon is partially or even significantly consumed (depleted) by the deposits, the increase in the CH\(_3\)Cl flow rate does not influence the efficiency of the deposit formation. Therefore, the additional supply of carbon species contributes to the growth rate in a straightforward manner [Fig. 5(a)]. By increasing the flow rate of SiH\(_4\) in the presence of HCl, the efficiency of the polycrystalline deposition was enhanced upstream. In the regions where the polycrystalline deposition coexists with the epitaxial growth, the \( R_g \) of the epitaxial process also increased at the more upstream regions of the growth zone due to the higher availability of Si [Fig. 5(b)]. However, since the polycrystalline deposits consume a very large amount of the precursors (not only Si but also carbon), the more downstream regions of the growth zone experience actually lower \( R_g \) at higher SiH\(_4\) flows [Fig. 5(b)]. However, the enhanced supply of SiH\(_4\) does not contribute to any significant increase in the polycrystalline deposition in the growth experiments without HCl, which is due to the quick capture of Si caused by the homogeneous gas-phase nucleation.

V. CONCLUSION

HCl was found efficient in dissociating clusters in the gas phase even at low epitaxial growth temperatures of 1300 °C and below. One result of such dissociation may be
an additional supply of not only silicon but also carbon for the epitaxial growth (especially at low HCl flow rates), which is consistent with the hypothesis that the gas-phase clusters are actually Si–Si$_x$C$_{1-x}$ complexes that predominantly consist of silicon but also certain amount of carbon at the cluster periphery.

The observation of the pattern of polycrystalline deposition in the upstream portion of the hot zone revealed how the etching of gas-phase clusters by HCl develops along the gas flow direction when approaching the hot susceptor and inside the susceptor close to the growth zone. At the low temperatures of the investigated epitaxial growth technique, HCl is working against Si vapor condensation as soon as the gas-phase clusters start to form (i.e., at least a few centimeters upstream from the growth zone). The clustering in the absence of HCl significantly reduces the extension of the upstream region where the polycrystalline deposition is observed (and consequently reduces precursor depletion by this mechanism). The addition of HCl makes this depletion more significant by dissociating those clusters. Polycrystalline deposition in the regions close to the growth zone during the growth with HCl also causes depletion of carbon species in addition to silicon.

Complex dependencies of the growth rate and the effective Si/C ratio on the HCl flow rate and the precursor flow rates, as well as lower than expected improvements caused by HCl, were explained with the help of the model of precursor-depletion by the polycrystalline deposition. It appears to be desirable to postpone the gas-phase cluster dissociation till entering the growth zone, where the released silicon (and possibly carbon) species would contribute to the epitaxial growth, thus enhancing the growth. Possible ways of influencing the gas-phase reaction kinetics in order to achieve this outcome are being investigated.

While the complex trends reported in this work quantitatively depend on the exact design of the epitaxial growth reactor (and the hot zone in particular) as well as on the growth conditions, the interpretations of these trends provided justifications for new growth mechanisms that may play an important role in a variety of reactor designs and growth conditions at low temperatures. Moreover, the hot-wall reactor design used in this work is fairly common for modern SiC epitaxial industry.

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