

# Chloride-Based CVD Growth of Silicon Carbide for Electronic Applications

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## 1. INTRODUCTION

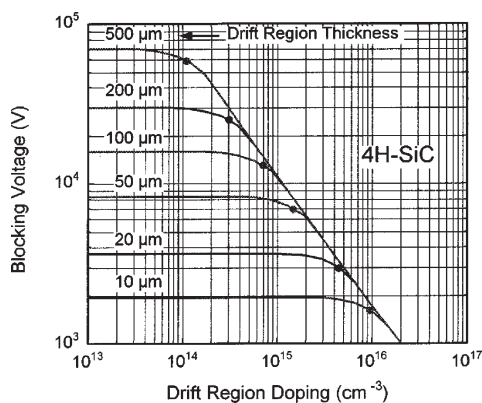
Silicon carbide (SiC) is a fascinating material. In one way, it is very simple; there are only two atoms building up the crystal—silicon and carbon, where each atom is sp<sup>3</sup>-hybridized and forms four bonds to four other atoms of the opposite kind. In another way, SiC is quite complicated; the crystal structure gives rise to polytypism, which is a one-dimensional polymorphism. More than 250 polytypes are predicted;<sup>1</sup> however, only a handful are studied in more detail, and in principle, only three are of major importance. Furthermore, SiC is a very hard material; on the hardness scale by Mohs, where talc is given 1 and diamond is given 10, SiC has 9.3.<sup>2</sup>

The first report of a compound containing silicon–carbon bonds was published 1824 by the Swedish chemist Jöns Jacob Berzelius,<sup>3</sup> and he is thus often referred to as the discoverer of SiC. However, it was the French chemist and Nobel laureate Henri Moissan who first discovered SiC in nature when in 1905 he investigated a meteorite from Cañon Diablo, AZ, USA.<sup>4</sup> In mineralogy, SiC is therefore also known as Moissanite.

The semiconducting properties of SiC were to some extent explored very early, since the very first report on electroluminescence from a crystal in 1907 reported a yellowish light from SiC crystals when subjected to electricity.<sup>5</sup> Today, those exceptional semiconducting properties are the motivation for the majority of the research on SiC. Silicon carbide is a semiconductor with a wide, indirect band gap of around 3 eV, depending on the polytype. It is well-known to have excellent material properties, such as high breakdown electric field strength, high saturated electron velocity, and high thermal conductivity, which make it a very attractive material for electronic devices for high-power, high-frequency, and high temperature applications. This gives SiC technology an edge over the Si technology in applications where high blocking voltages or high switching frequencies are required. Power electronics based on SiC can greatly reduce the power losses in most generation and distribution systems for electrical energy. The higher frequency, smaller dimensions, reduced cooling requirements, and greater efficiency obtained with SiC

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**Figure 1.** Blocking voltage of 4H-SiC epitaxial layers as a function of thickness and doping. Reprinted with permission from ref 6. Copyright 2002 IEEE.

power electronics will give more efficient systems in any application where the AC-DC, DC-AC, or DC-DC conversion is required.

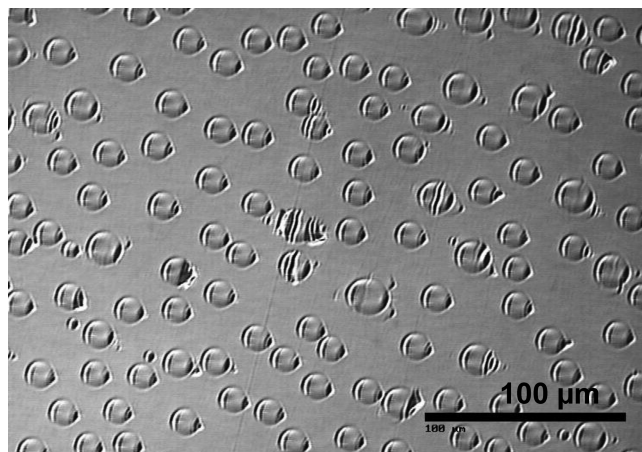
Fabrication of power devices always requires the growth of an epitaxial layer that will serve as the active layer and the contact layers. The thickness and doping of this active epitaxial layer will determine the blocking voltage of the device (Figure 1). As an example, a 5 kV blocking device will need an epitaxial layer approximately 50  $\mu\text{m}$  thick with a low n-type doping.<sup>6</sup>

Typically, SiC homoepitaxial growth is done using chemical vapor deposition (CVD) with silane ( $\text{SiH}_4$ ) as the silicon precursor and light hydrocarbons, *e.g.* ethylene ( $\text{C}_2\text{H}_4$ ) or propane ( $\text{C}_3\text{H}_8$ ), as the carbon precursor. Hydrogen gas, sometimes mixed with some argon, is used as carrier gas. The growth temperature and pressure are usually between 1500 and 1650  $^\circ\text{C}$  and 100–1000 mbar, respectively. The standard nonchlorinated chemistry for CVD of SiC has been extensively studied and reviewed elsewhere.<sup>7–12</sup>

The horizontal hot wall design of the susceptor is today the dominating design<sup>13</sup> in CVD applications for SiC growth, since it gives a more uniform heat distribution and better cracking efficiency of the precursors. The typical growth rate for SiC homoepitaxy is 5–10  $\mu\text{m}/\text{h}$ , thus making the growth of the epitaxial layer for power devices very time-consuming and thereby also very expensive. The long production time and high cost of these epitaxial layers are the main obstacles to overcome, in order to give to SiC power device technology its major breakthrough.

To increase the growth rate, the amount of precursors in the growth process must be increased, which unreservedly leads to problems with homogeneous nucleation in the gas phase due to the high partial pressures of the precursors. For the SiC epitaxial growth process, the main problem is the formation of silicon droplets. These droplets fall down on the substrate but normally evaporate quite quickly; however, their contact with the substrate will badly affect the growing epitaxial layer (Figure 2), making it useless for devices.

To circumvent the problem with the silicon droplets, one can take help from the principles of physics either by increasing the growth temperature to dissolve the silicon droplets with the higher amount of energy in the system<sup>14</sup> or by reducing the pressure of the process, thereby hindering the droplets to form due to the lower partial pressure of the silicon. Applying the former method at extreme temperatures leads to the operating principle of the high temperature CVD method for the production of bulk



**Figure 2.** Optical microscope view of a SiC epitaxial layer surface from a CVD process in which silicon droplets were formed.

SiC crystals.<sup>15</sup> The latter approach results in a higher gas velocity through the susceptor, which consequently means that any formed droplets will be transported out of the susceptor faster, decreasing the probability that they will come in contact with the substrate.<sup>16–18</sup>

A more elegant way is to utilize the principles of chemistry by preventing the formation of the silicon droplets through the addition of something to the gas mixture that binds more strongly to silicon than silicon. A good candidate to use here would be a halogen. The standard bond enthalpies for the Si–Si, Si–F, Si–Cl, Si–Br, and Si–I bonds are 226, 597, 400, 330, and 234  $\text{kJ mol}^{-1}$  or 2.34, 6.19, 4.15, 3.42, and 2.42 eV, respectively.<sup>19</sup> Fluorine is not a good candidate, since it would form HF in the process, which etches the quartz glass in the CVD reactor; neither is iodine, since it forms too weak bonds to Si to dissolve the droplets effectively. Therefore, the choice stands between chlorine and bromine. The fact that chlorinated compounds are already available in high purity and at low cost, due to their extensive use in the silicon industry, makes chlorine the obvious choice also for SiC.

This review strives to give a full overview of the work that has been done in the field of chloride-based CVD growth of SiC. Since the silicon industry, to a large extent, is a source of benchmarks as well as inspiration to the SiC community, a brief overview of the use of chlorinated chemistry for the growth of silicon homoepitaxial layers will be given in section 2. The main part of this review concerns the growth of SiC epitaxial layers; the various precursor approaches one can apply for chloride-based growth are reviewed in section 3. The work done on chloride-based bulk growth processes is reported in section 4. To obtain a deeper understanding of the chloride-based process, simulations is an invaluable tool (section 5), but also comparisons between different chlorinated chemistries (section 6) can provide much insight. Finally, the differences necessary for growth processes on different off-cut substrates will be addressed in section 7.

## 2. SHORT REMARKS ON CHLORIDE-BASED GROWTH OF SILICON HOMOEPITAXIAL LAYERS

Although the material properties of silicon differ from those of SiC, the silicon industry serves as a constant source of both benchmarks and inspiration to the SiC community. Hence, it is well worth mentioning a few words on the growth of silicon

homoepitaxial layers, since it was the silicon industry that started using chlorinated silicon compounds in the growth process and today chloride-based growth is totally dominating the field of silicon epitaxial growth. Chloride-based growth of silicon homoepitaxial layers was first reported by Theuerer in 1961,<sup>20</sup> where a CVD process with tetrachlorosilane ( $\text{SiCl}_4$ ) in hydrogen was used to deposit silicon epitaxial layers on silicon (111) substrates with a growth rate as high as  $300 \mu\text{m/h}$  at  $1270^\circ\text{C}$ . Also B- and P-doping were studied using  $\text{BBr}_3$  and  $\text{PCl}_3$ , respectively.

Today the majority of the silicon epitaxial layers is produced by some chloride-based process where silane ( $\text{SiH}_4$ ) molecules with two (dichlorosilane (DCS),  $\text{SiH}_2\text{Cl}_2$ ), three (trichlorosilane (TCS),  $\text{SiHCl}_3$ ), or four (tetrachlorosilane (TET),  $\text{SiCl}_4$ ) chlorine atoms are used; TCS and TET are liquids at room temperature, while DCS is a gas (boiling point:  $8.3^\circ\text{C}$ <sup>21</sup>). Normal silane with the addition of HCl is not commonly used in epitaxial growth of silicon. The use of DCS is mostly limited to reduced pressure processes at around 60–100 mbar. For atmospheric pressure processes, TCS is preferred over TET, but for high temperature processes at temperatures up to  $1300^\circ\text{C}$ , TET is easier to handle and gives less unwanted depositions in the reactor.<sup>22</sup>

The main use for HCl in silicon epitaxial growth is as an etching agent. Prior to growth, the wafer surface is etched with a small flow of HCl inside the CVD reactor to remove any silicon dioxide that might be present on the surface after the wet cleaning of the wafer. After growth, the reactor is cleaned with a large flow of HCl to remove any deposited silicon in the susceptor and quartz tube; a flow of several tens of liters per minute is used, and the etching rate can reach  $7 \mu\text{m/min}$ .<sup>23</sup>

It should be noted that the growth of silicon epitaxial layers is done at much lower temperatures ( $\sim 1000$ – $1200^\circ\text{C}$ ) than the growth of SiC epitaxial layers ( $\sim 1500$ – $1800^\circ\text{C}$ ). A lower growth temperature is adequate, since the silicon crystal is a much simpler crystal compared to SiC; silicon consists of only *one* type of atom that needs to be ordered into a lattice of a cubic structure that does not give rise to polymorphism. The upper limit of the process is obviously set by the melting point of silicon,  $1414^\circ\text{C}$ .<sup>24</sup> The high growth rate provided by the chloride-based growth chemistry, in the order of a few hundred  $\mu\text{m/min}$ , combined with the relatively low growth temperature, has allowed the development of the rapid thermal CVD (RT-CVD), which is done in a cold wall reactor; a single wafer is loaded into the growth zone from a cassette filled with wafers, and the growth zone is rapidly heated by IR lamps. In such a reactor, an epitaxial layer may be grown in a few minutes. The rapid heating and cooling rate are possible due to a very small thermal mass in the reactor, which makes the total processing time for each wafer very short.<sup>25</sup>

### 3. CHLORIDE-BASED GROWTH OF SILICON CARBIDE EPITAXIAL LAYERS

For the growth of SiC epitaxial layers using a chloride-based chemistry, one can choose from five main approaches to add chlorine to the gas mixture: (i) add a flow of HCl gas to the standard precursors silane and a hydrocarbon (*e. g.* propane or ethylene); (ii) replace the silane with a chlorinated silane molecule ( $\text{SiH}_x\text{Cl}_y$ ) while keeping the propane/ethylene; (iii) replace the carbon precursor with a chlorinated hydrocarbon molecule ( $\text{CH}_x\text{Cl}_y$ ) while keeping the silane; (iv) use a molecule

that contains silicon, carbon, and chlorine ( $\text{SiC}_x\text{Cl}_y\text{H}_z$ ); or (v) use a combination of a chlorinated silane molecule and a chlorinated hydrocarbon molecule ( $\text{SiH}_x\text{Cl}_y + \text{CH}_x\text{Cl}_y$ ). Results from all these approaches have been reported for homoepitaxial growth and are reviewed below.

#### 3.1. HCl Approach

Initially, HCl-gas was used together with hydrogen gas for etching the substrate surface prior to growth. The addition of HCl during the etch process increases the etching rate and produces a stepped surface,<sup>26–28</sup> which will favor step-flow growth. Chlorine interacts preferentially with the silicon atoms on the surface,<sup>29</sup> but an excess of it would deteriorate the surface, leaving behind etch pits. HCl was demonstrated to be very effective in prohibiting the formation of the cubic polytype of SiC (3C). Powell et al. demonstrated how an *in situ* HCl etch prior to the growth could remove the attachment sites on dislocations for 3C inclusions,<sup>30</sup> which is especially important for the growth on low off-angle 6H-SiC substrates. On the other hand, when the same etching was conducted at low temperatures on patterned substrates, a homogeneous 3C-SiC film could be grown.<sup>31</sup>

However, in these studies there was no HCl-flow during growth. The use of HCl as a growth additive was initially used as an etching agent *during* growth to etch away 3C inclusions during on-axis growth of 6H-SiC,<sup>32</sup> and the target in this study was not high growth rate but polytype stability.

**3.1.1. Homoepitaxial Growth.** The first papers on a chlorinated growth process with a high growth rate, developed on  $8^\circ$  off-axis 4H-SiC substrates, were reported during the European Conference on Silicon Carbide and Related Materials 2004 (ECSCRM04) when Crippa et al.<sup>33</sup> reported  $20 \mu\text{m/h}$  for a process with HCl added to the standard precursors in a hot-wall CVD reactor and Myers et al.<sup>34</sup> reported growth rates of  $28$  to  $55 \mu\text{m/h}$  for a similar process, albeit with a degraded morphology for the higher rates. The process was then further developed and an epitaxial growth process with a rate of  $112 \mu\text{m/h}$  was presented at the following International Conference on Silicon Carbide and Related Materials (ICSCRM) in 2005. Preliminary results from Schottky diodes made on those epitaxial layers were also reported.<sup>35,36</sup> Subsequently, at the ECSCRM06 (2006) further process development and high quality Schottky diode characteristics were reported.<sup>37,38</sup> The process has also been optimized by using results from optical and electrical characterization of the grown epitaxial layers.<sup>39</sup> The process stability has been studied using a demarcation technique by introducing a very high  $\text{N}_2$ -flow for 10 s every third minute and thereby creating very thin highly doped stripes in the material visible by SEM; these demarcation lines are evenly spaced in the epitaxial layer, showing that the growth rate is stable from the start and over time.<sup>40</sup>

The HCl approach has also been optimized for the growth on  $4^\circ$  off-axis 4H-SiC substrates where the growth of very high quality  $38 \mu\text{m}$  thick epitaxial layers on  $3''$  wafers was grown at  $7 \mu\text{m/h}$ ,<sup>41</sup> and an even higher growth rate of  $28 \mu\text{m/h}$  with high quality morphology has also been demonstrated.<sup>42</sup> Lately, the growth on  $4^\circ$  off-axis 4H-SiC substrates has been further developed, and a growth rate of about  $100 \mu\text{m/h}$  was achieved by adopting a HCl *in situ* etch step prior to the growth.<sup>43</sup> It was speculated that the HCl etching was needed to minimize the source of triangular defects, while growing at a moderately reduced growth temperature.

The growth on on-axis 4H- and 6H-SiC substrates has benefited the HCl addition in the process,<sup>44,45</sup> and a growth rate around 100  $\mu\text{m}/\text{h}$  has been reported also for growth on on-axis substrates, as further discussed below.

From the mentioned works,<sup>35–43</sup> it appears that a Cl/Si ratio between 3 and 5 is the optimum value to achieve a high quality homoepitaxial layer free of silicon droplet related defects. A lower amount of chlorine may be used,<sup>37</sup> but electrical characterization indicated a degradation of material quality. Report on epitaxial growth at a reduced carrier flow and process pressure<sup>46</sup> indicates that these conditions may require lower chlorine inputs due to the increased desorption of silicon species at lower pressure. The increased desorption combined with the etching of silicon atoms by the chlorine significantly increases the C/Si ratio at the surface. Thus, Cl/Si ratios in excess of 5 may result in a surface roughening and decrease of growth rate. When using the standard growth conditions with Cl/Si lower than or equal to 1, homogeneous nucleation in the gas phase could be noticed.<sup>37</sup> Surprisingly, when using a low pressure (15 mbar) process, no silicon droplet related defects were formed on the epitaxial layer at such low Cl/Si ratio, indicating that the chlorine content was high enough to prevent silicon aggregation.<sup>46</sup>

Low temperature homoepitaxial growth has been demonstrated by chloride-based CVD processes, as further described below. Using the approach of adding HCl to the standard precursors, 4H-SiC was homoepitaxially grown with a growth rate of 7.5  $\mu\text{m}/\text{h}$  at 1300 °C.<sup>47</sup> However, other chloride-based approaches were found to be more efficient and rendered smoother epitaxial layer morphologies as reported below.

**3.1.2. Heteroepitaxial Growth.** The use of the HCl approach for heteroepitaxial growth of 3C-SiC on silicon substrates was first reported in 1998 by Gao et al.;<sup>48</sup> they noticed an improved quality of the grown material when HCl was added. The improvement was explained by the increased etch rate of highly dislocated areas as compared to areas with high crystal perfection. This was evidenced by the fact that a lower growth rate was observed when HCl was added. It should be noted here that the studied Cl/Si was 50. In a more recent study, the HCl approach was used for the growth of 3C-SiC for MEMS applications.<sup>49</sup> There are reports on selective area growth of SiC using SiO<sub>2</sub> masks and addition of HCl to the gas mixture;<sup>50–52</sup> however, the grown material did not seem to be single crystalline. It is common to use HCl for a proper cleaning and *in situ* preparation of the substrate prior to the growth. Nishino et al. has reported several studies<sup>53,54</sup> of the growth of 3C-SiC on silicon substrates. A chlorinated silicon chemistry was usually selected for the precursors in the growth at the reduced temperature (below 1400 °C). Since chlorinated silicon precursors were usually adopted, HCl was only introduced for etching in the temperature range 1100–1200 °C. A further carbonization step was required to grow high quality 3C layers, which has been shown to be the only parameter which really mattered to obtain such results.

**3.1.3. Growth of Cubic SiC on Hexagonal SiC.** Traditionally, the cubic 3C-SiC polytype has been grown on silicon substrates, since there are no high quality 3C-SiC-substrates available; however, the mismatches in lattice constant and thermal expansion have limited the thickness and quality of the grown 3C-SiC epitaxial layers. Heteropolytypic epitaxial growth of 3C-SiC on 6H-SiC would permit the growth of thicker layers and higher quality and, thus, be an important step toward the commercialization of the 3C-SiC polytype. Growth of 3C-SiC on

6H-, 4H-, and 15R-SiC<sup>55–57</sup> has been demonstrated using the standard, nonchlorinated chemistry. Early attempts of growing 3C on 6H with chloride-based chemistry were presented in 2000<sup>58</sup> when the HCl approach was used. However, a very high Cl/Si ratio of 50 was used, and thus, the sole effect the addition of HCl had was only found to decrease the growth rate. The growth of very high quality, 10  $\mu\text{m}$  thick 3C-SiC epitaxial layers grown at 10  $\mu\text{m}/\text{h}$  has been reported by using the HCl approach; also 80  $\mu\text{m}$  thick layers grown at 160  $\mu\text{m}/\text{h}$  were reported; however, the latter very high growth rate led to an increased stress in the material and thereby a lower material quality.<sup>59</sup>

## 3.2. SiH<sub>x</sub>Cl<sub>y</sub> Approach

As previously mentioned, chlorosilanes are the most frequently used precursors for the epitaxial growth of silicon epitaxial layers. The most commonly used chlorosilanes are TCS (SiHCl<sub>3</sub>) and TET (SiCl<sub>4</sub>), which advantageously also may be employed for SiC growth by simply adding a carbon source, e.g. a hydrocarbon. This was shown already in 1909, when SiC deposition from the vapors of SiCl<sub>4</sub>/SiHCl<sub>3</sub> together with benzene was reported;<sup>60</sup> however, the deposited material was a polycrystalline powder. Using chlorinated silane molecules, the Cl/Si ratio is fixed within the range 1–4, and in principle, no HCl is required, unless specific *in situ* etching with chlorine or higher Cl/Si ratios is desired. Some may consider the fact that TCS and TET are liquids at room temperature to be a disadvantage, since they require either a bubbler system or a heated precursor bottle with heated gas-lines and mass flow controllers. At high growth rates, care must be taken to avoid cooling of the liquid when using a bubbler for TCS or TET. The thermal control of the liquid is an issue that must be handled which is just as important as the flow through the bubbler.

**3.2.1. Homoepitaxial Growth.** The approach to use a chlorinated silane molecule instead of normal silane in a homoepitaxial SiC growth process was reported already in 1975,<sup>61,62</sup> when Matsunami and co-workers used tetrachlorosilane, SiCl<sub>4</sub> (TET), together with propane for the epitaxial growth of 6H-SiC at growth rates up to 12  $\mu\text{m}/\text{h}$ . This process was also used to grow epitaxial layers for the fabrication of blue light emitting diodes.<sup>63</sup> The use of TET together with hexane (C<sub>6</sub>H<sub>14</sub>)<sup>64</sup> for homoepitaxial growth of 6H-SiC was also demonstrated at 1850 °C with a growth rate of 3.6–7.2  $\mu\text{m}/\text{h}$ . More recently, TET has been used together with propane at high temperatures, up to 1850 °C, in a hot-wall CVD reactor. Growth rates up to 200  $\mu\text{m}/\text{h}$  were reported, and the material was of high crystalline quality. The dependence of the growth rate on temperature was also reported.<sup>65,66</sup> The structural defects in the grown epitaxial layers were subsequently studied using X-ray topography.<sup>67</sup> Homoepitaxial growth of SiC using tetrachlorosilane and propane has also been tested at low temperatures (1300 °C), where 4H-SiC was successfully grown with a low growth rate of 2–3  $\mu\text{m}/\text{h}$ .<sup>68</sup>

The use of trichlorosilane, SiHCl<sub>3</sub> (TCS), was first reported in 2005,<sup>69</sup> where TCS and ethylene were used as precursors in a hot-wall CVD reactor process yielding a growth rate of 16  $\mu\text{m}/\text{h}$ . This process was further developed and growth rates in excess of 100  $\mu\text{m}/\text{h}$  were reported.<sup>38</sup> In a later study, the successful growth of 100  $\mu\text{m}$  thick layers grown on 8° off-axis substrates and 40  $\mu\text{m}$  thick layers grown on 4° off-axis substrates was reported.<sup>70,71</sup> The TCS-process has also been used to grow thin device structures with very abrupt junctions.<sup>72</sup>

In a recent report, the growth of 4H SiC on  $8^\circ$  off axis substrates was performed using dichlorosilane,  $\text{SiH}_2\text{Cl}_2$  (DCS), and propane as precursors in a chimney CVD reactor.<sup>73</sup> Growth rates up to  $100 \mu\text{m/h}$  with very high crystalline quality were achieved at  $1750^\circ\text{C}$ .

Monochlorosilane,  $\text{SiH}_3\text{Cl}$ , has also been used together with propane in a hot-wall CVD reactor. Initially, a growth rate of  $20 \mu\text{m/h}$  together with device results were reported,<sup>74</sup> and the process was then later scaled up to work in a multiwafer ( $5 \times 3''$ ) CVD reactor, producing  $20\text{--}30 \mu\text{m}$  thick epitaxial layers of very high quality.<sup>75</sup>

Most processes for the homoepitaxial growth of SiC at standard temperatures ( $1500\text{--}1600^\circ\text{C}$ ) and on off-axis substrates use a Cl/Si ratio between 3 and 5. This makes TCS or TET ideally suited for the epitaxial deposition of SiC layers. Using either of these, homogeneous nucleation of silicon has never been reported in the gas phase, contrary to what is reported when HCl is added to the standard silane and ethylene chemistry.<sup>37</sup> This is most likely due to the different chemistry of the chlorosilanes compared to normal silane plus HCl for the formation of intermediates in the gas phase.

**3.2.2. Heteroepitaxial Growth.** It is interesting to note that chlorosilanes ( $\text{SiCl}_4$ ,<sup>53</sup>  $\text{SiHCl}_3$ ,<sup>76,77</sup> and  $\text{SiH}_2\text{Cl}_2$ <sup>78</sup>) were to a great extent used for heteroepitaxial growth of SiC on Si (especially in the 1980s) by several groups. Their usage was limited and soon abandoned when high purity silane became commercially available at a low price. More recent papers report monocrystalline cubic SiC growth on Si substrates; since these processes are run at temperatures below  $1400^\circ\text{C}$ , DCS and TCS, which have lower decomposition temperatures, are preferred over TET. Heteroepitaxial growth of single crystal SiC on large diameter silicon wafers has been reported by using DCS<sup>79</sup> and TCS on patterned or pretreated substrates<sup>80</sup> and on  $6''$  Si-substrates.<sup>81,82</sup> Growth of 3C-SiC on Si by using TCS has further been studied on various Si-substrate orientations,<sup>83</sup> and the effect of the growth rate on the film quality has also been studied.<sup>84</sup> Also, selective area growth of 3C-SiC on  $\text{SiO}_2$  masked Si has been reported using a low temperature ( $900\text{--}1000^\circ\text{C}$ ) process with DCS and an addition of HCl.<sup>85,86</sup>

### 3.3. $\text{CH}_x\text{Cl}_y$ Approach

The approach to supply chlorine to the process through the use of a chlorinated hydrocarbon was first proposed by Dr. Colin Wood in 2004,<sup>87</sup> and it is the least explored approach to chloride-based CVD growth of SiC. However, this approach has been proven successful at low temperature growth.

**3.3.1. Standard Temperature Growth.** The interest in a chlorocarbon precursor replacing the traditional hydrocarbons (e.g., propane) was inspired by the possibility of an alternative way to bring Cl in the system to suppress homogeneous nucleation of Si in the gas phase and a speculation that intermediate Cl-containing products of chlorocarbon decomposition may be different enough from those formed during HCl- or  $\text{SiH}_x\text{Cl}_y$ -based growth to enable different surface reactions.

In the earlier years, chloromethane was utilized in diamond growth<sup>88</sup> as well as in growth of heteroepitaxial 3C-SiC.<sup>89</sup> The first attempt to utilize chloromethane for homoepitaxial growth of 4H-SiC material was reported in 2004,<sup>90</sup> which was followed by a more detailed investigation of the growth trends and comparison between the chlorocarbon and hydrocarbon growth.<sup>91</sup> The growth experiments were conducted in a low-pressure hot-wall CVD reactor at  $1600^\circ\text{C}$  and 400 Torr, which

was the typical pressure commonly used in this reactor for the traditional  $\text{C}_3\text{H}_8$ -based homoepitaxial growth of 4H-SiC. Hydrogen gas was used as the carrier gas, and  $\text{SiH}_4$  (3% in  $\text{H}_2$ ) was used as the silicon source. Due to easy handling, chloromethane ( $\text{CH}_3\text{Cl}$ ), a gas at room temperature, was selected as the chlorocarbon precursor to replace  $\text{C}_3\text{H}_8$ .

Typical growth experiments with nonchlorinated chemistry and  $\text{C}_3\text{H}_8$  as carbon precursor in the reactor used in ref 90, aiming at a growth rate of around  $3\text{--}4 \mu\text{m/h}$ , were characterized by the observation of a visible Si vapor trail downstream of the hot zone as well as inside the hot-wall susceptor when viewed from the rear port of the reactor. However, no apparent changes in the appearance of the Si vapor trail could be observed when  $\text{CH}_3\text{Cl}$  replaced  $\text{C}_3\text{H}_8$ .

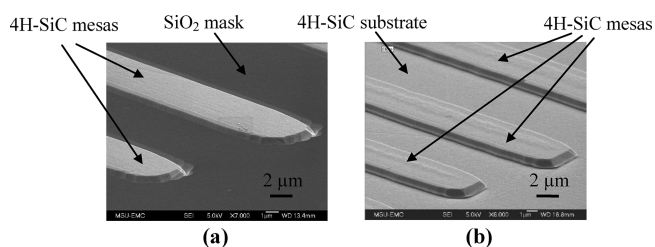
Only a relatively modest effect of  $\text{C}_3\text{H}_8$  replacement with  $\text{CH}_3\text{Cl}$  was observed in the experiments conducted at the traditional growth temperatures,  $1600^\circ\text{C}$  and above. The effect from the use of  $\text{CH}_3\text{Cl}$  was limited to the changes of the reaction kinetics and a significant increase of the growth rate for the same  $\text{SiH}_4$  flow rate and the C/Si ratio at the investigated growth conditions. However, the maximum growth rate before morphology degradation doubled, from below  $10 \mu\text{m/h}$  to more than  $20 \mu\text{m/h}$ , when the temperature was increased from  $1600$  to  $1700^\circ\text{C}$ .<sup>91</sup>

**3.3.2. Low Temperature Growth.** Much more extensive investigations of the homoepitaxial growth with the chlorocarbon precursor  $\text{CH}_3\text{Cl}$  (further referred to as chlorocarbon epitaxial growth) were conducted at untraditionally low growth temperatures. Previous studies with HCl-additions to the SiC growth process on on-axis substrates showed promising effects of Cl-addition to improve surface reactions and suppress 2D nucleation on large terraces of low-off-angle surfaces.<sup>32</sup> The same Cl-related improvement mechanisms were expected to be beneficial for growth on off-axis substrates at low temperatures.

The use of  $\text{CH}_3\text{Cl}$  precursor enabled growth of electronic-quality 4H-SiC epitaxial layers with nitrogen and aluminum concentrations from secondary ion mass spectrometry (SIMS) below  $10^{16}$  and  $10^{15} \text{cm}^{-3}$ , at temperatures as low as  $1300^\circ\text{C}$ . However, the maximum growth rate that could be achieved without morphology degradation decreased when reducing the growth temperature. Using the optimized growth conditions, specular epitaxial layer surface morphology could be achieved even at  $1300^\circ\text{C}$ , however, at a growth rate of no more than  $2.5\text{--}3 \mu\text{m/h}$ .<sup>92,93</sup>

The growth mechanisms responsible for the morphology degradation when attempting an increase of the growth rate at  $1300^\circ\text{C}$  beyond  $3 \mu\text{m/h}$  were investigated.<sup>92</sup> The dependence on the C-supply was found to deviate from the conventional behavior normally observed during the higher-temperature growth of SiC. It was suggested<sup>92</sup> that most of the excess silicon vapor, beyond a critical concentration (which is proportional to the temperature), was converted into clusters in the low-temperature chlorocarbon epitaxial growth. As a result, when one attempts to increase the growth rate by increasing the Si and C precursor flow rates while maintaining the fixed value of the input C/Si ratio, the effective (real) value of the C/Si ratio at the growth surface actually increases; any additional supply of Si could not reduce the effective C/Si. Therefore, an unfavorably high value of the C/Si ratio was unavoidable at high growth rates, causing the morphology deterioration.

The addition of HCl to the low temperature  $\text{CH}_3\text{Cl}$  process caused significant reduction, though not complete elimination, of



**Figure 3.** Low-temperature selective epitaxial growth of 4H-SiC at 1300 °C using a SiO<sub>2</sub> mask: (a) before and (b) after removing the SiO<sub>2</sub> mask. Reprinted with permission from Krishnan et al. Ref 99. Copyright 2007 Trans Tech Publications.

the Si vapor cloud inside the susceptor, which was attributed to the reduced homogeneous nucleation.<sup>94,95</sup> The growth rate was also increased from 5 to 7 μm/h by the addition of HCl. The reduced homogeneous nucleation leads to an increase of Si in the gas phase, and accordingly, the Si growth species got subsequently depleted, evidenced by the enhanced formation of Si-rich polycrystalline deposits, which were identified at the upstream portion of the hot zone when HCl addition was used.<sup>95</sup>

It was observed that the low growth temperature used in these processes leads to an increased number of surface defects on the grown epitaxial layers but also that HCl addition to the process decreased the number of basal plane dislocations propagating from the substrate into the epitaxial layers.<sup>96</sup> A major part of the surface defects are triangular defects. It has been shown that microscopic polycrystalline Si islands are formed on the substrate at these low growth temperatures and that they serve as nucleation centers for triangular defects.<sup>97</sup>

One of the clear advantages of a low temperature CVD process for SiC epitaxial layers is the possibility to have selective area growth by the use of SiO<sub>2</sub> masks. This has been realized by using the CH<sub>3</sub>Cl process at 1300 °C (Figure 3). Although the purpose was the fundamental study of the growth at low temperatures, it still shows the potential for using selective growth in SiC device fabrication.<sup>98–100</sup>

### 3.4. SiH<sub>x</sub>C<sub>y</sub>Cl<sub>z</sub> Approach

The SiH<sub>x</sub>C<sub>y</sub>Cl<sub>z</sub> approach, *i.e.* use a precursor molecule that contains silicon, carbon, and chlorine, opens up the possibility to grow SiC *via* chloride-based chemistry using a single molecule as precursor. This has the obvious drawbacks of fixed C/Si and Cl/Si ratios disabling the fine-tuning of doping and morphology with these process parameters. This problem can, however, be somewhat overcome by the addition of more carbon and/or chlorine by *e.g.* C<sub>2</sub>H<sub>4</sub> and HCl, respectively. The molecule of choice for this approach has been methyltrichlorosilane, SiCH<sub>3</sub>Cl<sub>3</sub>, often abbreviated MTS, and as we will see, high quality material has been grown with very high growth rates using this molecule. The MTS molecule is also very often used when depositing hard, polycrystalline, ceramic SiC coatings; see *e.g.* refs 101–103. However, a detailed review of this field is beyond the scope of this paper, since the growth conditions for epitaxy differ from the conditions of polycrystalline growth; epitaxial growth requires higher temperature and lower supersaturation in the gas phase. MTS has also been used as precursor for the growth of (small, needle-like) single crystals of 2H-SiC,<sup>104</sup> and this process has been used to produce samples for fundamental studies of this rare SiC polytype.<sup>105</sup>

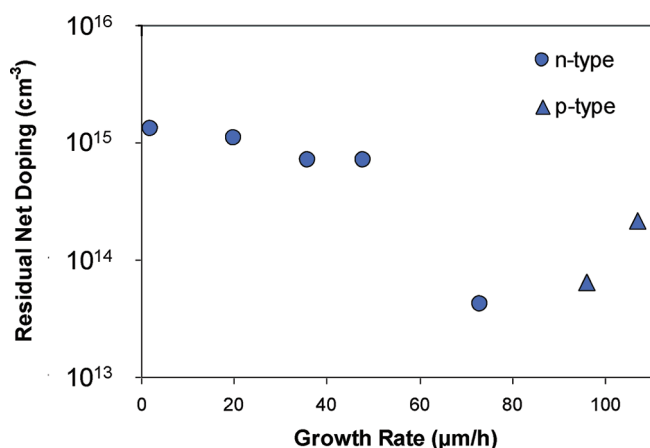
Since the growth of SiC using MTS has attracted so much interest, particularly for the use of SiC as hard coatings, several studies aiming to understand fundamental chemical aspects of the deposition of SiC from MTS have been conducted. Studies of what happens in the gas phase, both by using theoretical calculations of the decomposition of the MTS molecule<sup>106–111</sup> and by using thermodynamic calculations, for decomposition at temperatures up to 2000 K together with analysis of the process exhaust gases by gas chromatography,<sup>112</sup> have been done. All studies agree on one thing; the Si–C bond in the MTS molecule breaks, so there will not be any species having a Si–C bond which will build up the crystal as one might be tempted to think.

**3.4.1. Homoepitaxial Growth.** The use of a single molecule approach for homoepitaxial chloride-based growth of SiC was first reported already in 1969<sup>113</sup> when MTS was used to grow 3C-SiC epitaxial layers on solution grown 3C-SiC crystals. Epitaxial growth was achieved, and the authors found that better morphology and a more stable growth process were achieved using MTS rather than silane plus propane; however, the authors could not explain why the process improved when using MTS. They reported growth rates up to 20 μm/h, although the best morphology was achieved at growth rates of a few micrometers per hour.

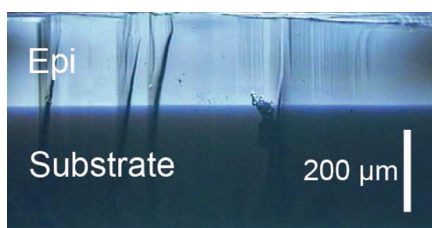
The first reports of homoepitaxial growth of hexagonal SiC from MTS were published in 1988, where etching and growth of 6H-SiC were studied using tungsten or molybdenum heaters,<sup>114</sup> and in 1995, where 6H-SiC was grown in a hot wall CVD reactor<sup>115</sup> and a growth rate of around 30 μm/h was reported.

The first report of a high growth rate process using MTS was done by Lu et al. in 2005,<sup>116</sup> where MTS was used to grow 4H- and 6H-SiC homoepitaxial layers on both on-axis and 3.5° and 8° off-axis substrates in a cold wall CVD reactor. The authors found that a temperature of 1600–1650 °C was needed for a smooth morphology, and they also found a linear relationship for the growth rate dependence of the MTS flow, and a maximum growth rate of up to 90 μm/h was achieved. Studies of the surface morphology and structural defects dependence on the H<sub>2</sub>/Ar ratio of the carrier gas were later published by the same group,<sup>117</sup> where a low H<sub>2</sub>/Ar of 0.1 was found to smoothen the surface while a H<sub>2</sub>/Ar of 0.2 was to be preferred, since it minimized the amount of basal plane dislocations replicating from the substrate into the epitaxial layer. The results were explained by the changes in the C/Si ratio of the process due to hydrogen etching on the graphite susceptor.

The first report on homoepitaxial growth of 4H-SiC in a hot wall CVD-reactor using standard 8° off cut 4H-SiC substrates was published in 2007,<sup>118</sup> and a growth rate up to 104 μm/h was reported. In a more detailed study,<sup>119</sup> the background doping dependence on the growth rate was studied and the doping was found to switch from n-type to p-type at around 80 μm/h (Figure 4). The addition of silane and/or ethylene allowed studies of the growth rate and the background doping dependence of the C/Si and Cl/Si ratios (although in a quite narrow range). The C/Si ratio makes the background doping switch from n-type (Si-rich growth) to p-type (C-rich growth), as seen in growth using standard chemistry.<sup>120</sup> The growth rate was found to decrease with lower C/Si; that is, the growth became carbon limited (also, this is found for the standard chemistry<sup>121</sup>). By using MTS as the single precursor for growth on 8° off axis 4H-SiC substrates, a growth rate as high as 170 μm/h has been demonstrated<sup>122</sup> as well as growth of 200 μm thick epitaxial layers (Figure 5) with 4.0 × 10<sup>14</sup> cm<sup>-3</sup> n-type background



**Figure 4.** Doping dependence of GR for growth of 4H-SiC using MTS as precursor. Reprinted with permission from ref 119. Copyright 2007 Elsevier B. V.

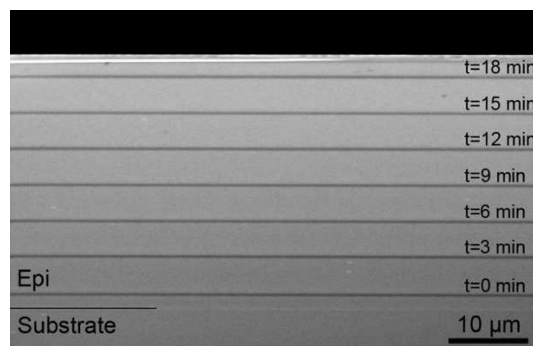


**Figure 5.** Cross section of a 200  $\mu\text{m}$  thick 4H-SiC epitaxial layer in an optical microscope; the epitaxial layer was grown from MTS with a growth rate of 100  $\mu\text{m}/\text{h}$ . Reprinted with permission from ref 123. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

doping, as measured by capacitance–voltage (CV) and photoluminescence (PL), and very high crystalline quality, grown in a 2 h process at 100  $\mu\text{m}/\text{h}$ ,<sup>123</sup> demonstrating the longtime stability of the process and the possibility to grow the very thick epitaxial layers needed for very high voltage power devices.<sup>6</sup> The growth rate stability over time was also demonstrated by using nitrogen demarcations, as described above. A SEM micrograph of this layer (Figure 6) showed very thin, highly doped regions, seen as darker lines, evenly spaced along the growth direction, indicating that the growth rate is stable from the start and over time.<sup>124</sup>

The epitaxial growth on on-axis substrates benefited by the use of MTS for homoepitaxial growth at high growth rates. The first approach used was to suppress the formation of heteropolytypical inclusions through the addition of extra HCl to the MTS and thereby growing at a higher Cl/Si ratio. With this approach, growth rates up to 20  $\mu\text{m}/\text{h}$  were achieved.<sup>125</sup> The second approach was to have a proper *in situ* surface preparation<sup>126</sup> prior to the growth. Combining the MTS chemistry with this, proper surface preparation growth rates as high as 105  $\mu\text{m}/\text{h}$  were demonstrated on on-axis substrates.<sup>45</sup>

The MTS approach has also been tested in the low temperature range (1300–1500 °C) and shown to be successful for homoepitaxial growth of 4H-SiC at 1300 °C. However, additions of extra ethylene and HCl to adjust the C/Si ratio to 1.35 and the Cl/Si ratio to 15 were needed; smooth epitaxial layers were grown under these conditions with a growth rate of 13  $\mu\text{m}/\text{h}$ .<sup>47</sup>



**Figure 6.** Cross section SEM micrograph of a 4H-SiC epitaxial layer grown from MTS at 100  $\mu\text{m}/\text{h}$  with short pulses of  $\text{N}_2$  introduced every third minute. The evenly spaced demarcation lines show that the growth rate is stable over time. Reprinted with permission from ref 124. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

**3.4.2. Heteroepitaxial Growth.** Heteroepitaxial growth of SiC is mainly done on silicon substrates, and it is then the cubic 3C polytype of SiC that is obtained. The melting point of silicon sets here an upper temperature limit to 1410 °C, and the use of a single molecule precursor has been motivated by the necessity to lower the process temperature.

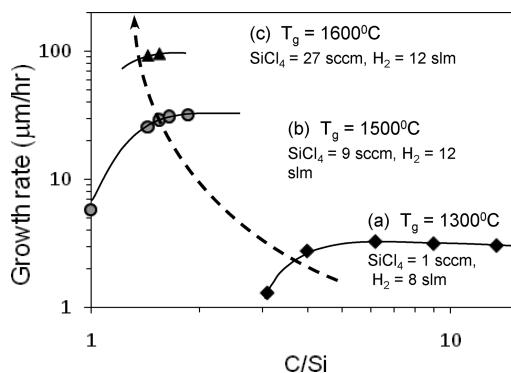
At the First International Conference on Amorphous and Crystalline Silicon Carbide and Related Materials in Washington, DC, in 1987, Nishino and Saraie reported the growth of single crystalline 3C-SiC on silicon substrates by using MTS as the sole precursor.<sup>127</sup> A few years later, Chiu et al. published a paper on the growth of epitaxial layers with a highly preferred orientation in a low pressure hot wall CVD reactor.<sup>128</sup>

In 1995 Kunstmann et al. reported the use of several brominated single molecule SiC precursors in comparison to MTS. They used a cold-wall CVD reactor and found a lower activation energy and higher growth rate for methyltribromosilane than for MTS; however, the material was of lower quality, most likely due to the lower quality of the methyltribromosilane which they synthesized themselves.<sup>129,130</sup> By using MTS, they were also able to eliminate the use of a carbonized buffer layer in the growth.<sup>131</sup> The MTS process was further developed, and a new temperature profile during the initial stage of the growth led to improved quality of the grown material and decreased interfacial stress; epitaxial layers as thick as 100  $\mu\text{m}$  were demonstrated.<sup>132</sup> Studies of the initial stage of the growth were done by growing very thin layers, 3–1200 nm,<sup>133</sup> and also pseudomorphic growth (growth where the epitaxial layer adopts the crystal structure of the substrate rather than its normal crystal structure) of very thin epitaxial layers has been reported.<sup>134</sup>

In a more recent paper, the growth of 3C-SiC using MTS on Si substrates was again investigated and several micrometers thick films with good morphology and surface adhesion were grown; however, they were reported to be polycrystalline.<sup>135</sup>

To study the kinetics of the growth of 3C-SiC on Si *in situ*, growth was done in a thermogravimeter equipped with a hot-wall CVD reactor, and the growth rate dependence on temperature and MTS pressure was investigated. It was found that the growth rate was limited by surface reactions at lower temperatures and by vapor mass transfer at higher temperatures. The limiting kinetic process changed at a critical temperature of about 1300 °C.<sup>136</sup>

Growth of 3C-SiC from MTS has also been done on graphite substrates which then allow higher growth temperatures, enabling



**Figure 7.** Growth rate versus C/Si ratio at (a) 1300 °C, (b) 1500 °C, and (c) 1600 °C. The  $\text{SiCl}_4$  flows used in parts a, b, and c correspond to roughly the highest growth rate before morphology degradation. The  $\text{H}_2$  flow was also adjusted with temperature to keep the growth rate homogeneity from upstream to downstream. Reprinted with permission from ref 142. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

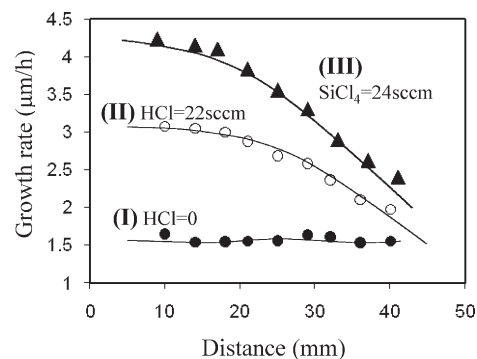
the growth of large (several  $\text{mm}^2$ ) single crystals; however, the growth is no longer epitaxial. This was reported already in 1967, when 0.5 mm thick yellow transparent crystals of 3C-SiC were grown on graphite<sup>137</sup> and used for optical studies of the band structure of 3C-SiC. Later, the growth of even thicker crystals ( $\sim 1.5 \text{ mm}$ ) with a very high crystalline quality was reported.<sup>138</sup> The field of 3C-SiC single crystal growth on graphite using MTS is reviewed in ref 139.

### 3.5. $\text{SiH}_x\text{Cl}_y + \text{CH}_x\text{Cl}_y$ Approach

The approach to mix a chlorinated silane and a chlorinated hydrocarbon was first reported in 1966 when a mixture of  $\text{SiCl}_4$  and  $\text{CCl}_4$  was used for the homoepitaxial growth of 6H-SiC crystals with a growth rate up to 40  $\mu\text{m/h}$  at 1600–1775 °C.<sup>140,141</sup> More recently, this approach has been revisited using the combination of  $\text{SiCl}_4$  and  $\text{CH}_3\text{Cl}$  at both standard and low temperatures.

**3.5.1. Standard Temperature Growth.** Homoepitaxial growth of 4H-SiC at standard temperatures (1500–1600 °C) with  $\text{SiCl}_4$  and  $\text{CH}_3\text{Cl}$  has been studied.<sup>142,143</sup> A linear dependence of the growth rate on the  $\text{SiCl}_4$  flow rate at 1600 °C was observed, for Si/ $\text{H}_2$  ratios up to 0.25%, with the growth rate close to 100  $\mu\text{m/h}$  at the highest Si/ $\text{H}_2$  ratio studied. The high quality of the epitaxial layers grown at 1600 °C and 95  $\mu\text{m/h}$  was confirmed by low-temperature photoluminescence spectroscopy, time-resolved luminescence, and high-resolution X-ray diffraction. The effect of temperature was also studied, and the reduction of the growth temperature from 1600 to 1300 °C (Figure 7, curves c to a) showed a drastic increase in the value of the effective C/Si ratio corresponding to the knee-point separating the Si- and C-supply limited modes. Higher input values of the C/Si ratio were required at lower temperature to enter the Si-supply limited mode. It is speculated that this behavior is caused by kinetic effects on the carbon chemistry at low growth temperature.

**3.5.2. Low Temperature Growth.** The low temperature process for the homoepitaxial growth of 4H-SiC with  $\text{CH}_3\text{Cl}$  as carbon source described above has been further studied under conditions where more chlorine was added to the system through the use of  $\text{SiCl}_4$  instead of  $\text{SiH}_4$ . Specifically, the ability of the  $\text{SiCl}_4$  precursor to suppress homogeneous nucleation was explored. When replacing  $\text{SiH}_4 + \text{HCl}$  with  $\text{SiCl}_4$ , an improvement



**Figure 8.** Growth rate at 1300 °C using three different precursor systems as a function of the distance from the leading edge of the growth zone.  $\text{CH}_3\text{Cl}$  was used as the C precursor in all three cases. The differences were as follows: (I)  $\text{SiH}_4 = 24 \text{ sccm}$  without HCl; (II) the same  $\text{SiH}_4$  flow with HCl added; and (III)  $\text{SiH}_4 + \text{HCl}$  is replaced with  $\text{SiCl}_4$ . Reprinted with permission from ref 145. Copyright 2010 Elsevier B. V.

in the morphology was noted, most likely due to different kinetics of decomposition of the Si precursor in the hot zone.<sup>144</sup> A growth rate of 5–6  $\mu\text{m/h}$  at 1300 °C was reported; however, the triangular defects appeared at increasingly higher concentrations above 3  $\mu\text{m/h}$ .<sup>145</sup> No Si vapor cloud and no deposit on the quartz walls was observed in the experiments with  $\text{SiCl}_4$ . The growth rate homogeneity resembled the result of the HCl-based experiments (Figure 8, curves (II) and (III)). An analysis of the trend of appearance and amount of polycrystalline SiC deposits in the upstream portion of the hot-zone in the experiments with HCl and  $\text{SiCl}_4$  was made. Judging by these polycrystalline deposits, it was the precursor depletion that was responsible for the observed lack of homogeneity in both cases.

It was suggested<sup>145</sup> that not all C-related species participate in the surface reactions of the epitaxial growth of SiC, thereby leading to a lowering of the effective C/Si ratio, which called for the use of high values of the input C/Si ratio. This behavior could be the origin of the superiority of  $\text{CH}_3\text{Cl}$  as the carbon precursor to achieve good epitaxial layer morphology at low growth temperatures, which is much more difficult (if not impossible) to do when using more traditional hydrocarbon precursors, such as propane. This hypothesis was further studied in refs 68 and 146, where a comparison between processes with  $\text{CH}_3\text{Cl}$  or  $\text{C}_3\text{H}_8$  used as carbon precursors was done, and the differences in the growth chemistries will be reviewed below.

### 3.6. Doping and Deep Level Defects in SiC Epitaxial Layers during Chloride-Based Growth

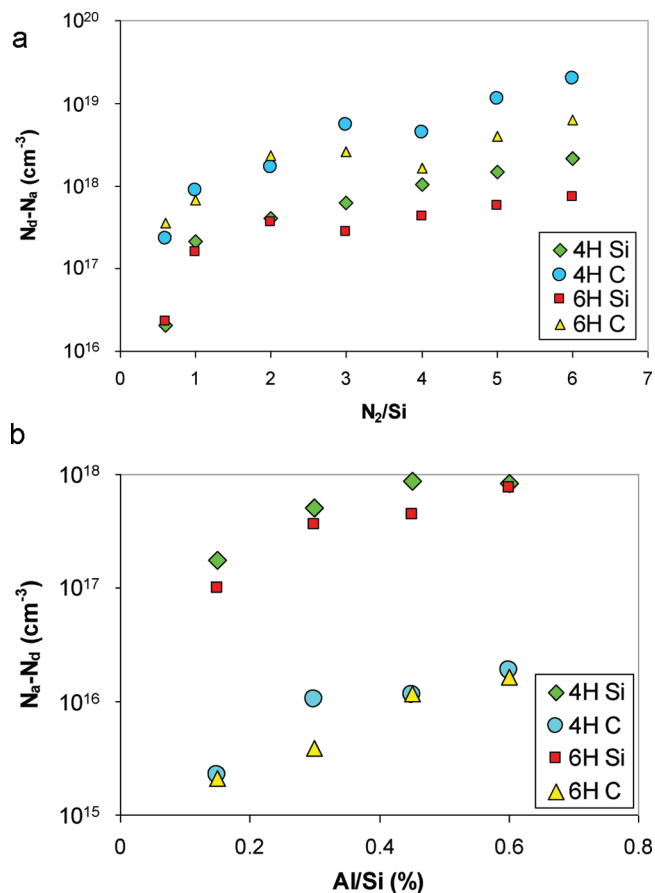
As mentioned above, the addition of HCl to the CVD process was first used for etching purposes prior to the growth. As a result of the HCl etching prior to growth, a reduction of the unintentional aluminum spike at the layer/substrate interface was observed.<sup>147</sup> A reduced compensation of the grown epitaxial layer was also noticed after the in situ HCl etching. Hence, HCl etching was believed to be very efficient to reduce the memory effect from both Al and B in homoepitaxial growth of SiC.<sup>148</sup> However, very few investigations have been carried out to understand the effect of the chlorine addition to the SiC CVD process on the incorporation of donor and acceptor atoms. Chlorine incorporation in the grown material is also an important consideration, and chlorine has indeed been detected in



polycrystalline layers grown from MTS at 1100 °C using parallel electron-energy-loss spectroscopy (PEELS).<sup>149</sup> However, in analysis of monocrystalline epitaxial layers, grown with the standard chemistry after HCl in situ etching<sup>148</sup> or grown with chloride-based chemistry using MTS,<sup>123</sup> using secondary ion mass spectrometry (SIMS), the chlorine content was found to be at the detection limit ( $1 \times 10^{14} \text{ cm}^{-3}$ ) of the SIMS measurement, suggesting that Cl atoms do not incorporate into the SiC lattice.

**3.6.1. Unintentionally Doped Layers.** The net background doping concentration in chloride-based processes has been reported to be in the same range as for standard epitaxial growth processes; however, the background conductivity of the grown 4H-SiC epitaxial layers was found to switch from n-type to p-type when the growth rate was increasing beyond roughly 80  $\mu\text{m/h}$  using the MTS approach (Figure 4).<sup>119</sup> Similar behavior was observed when using the HCl approach or a combination of both the MTS and HCl approaches.<sup>45</sup> However, this turning point (at about 80  $\mu\text{m/h}$ ) depends also on the other growth parameters, such as the C/Si and Cl/Si ratios and/or temperature. P-type conductivity with a background doping level up to the mid  $10^{15} \text{ cm}^{-3}$  has been observed.<sup>45,74</sup> Lower temperatures, lower Cl/Si ratios, higher growth rate, and C/Si ratio favor p-type conductivity. A suggested explanation for this behavior in background doping is that the effective C/Si ratio on the surface changes with growth rate; that is, the higher the growth rate, the faster the silicon atoms are consumed at the surface, which leads to a higher C/Si ratio and a higher incorporation of aluminum and boron.<sup>150</sup> A photoluminescence experiment on p-type layers reveals the presence of hydrogen-related lines in the PL spectrum,<sup>150,151</sup> which typically could indicate more incorporation of boron atoms.

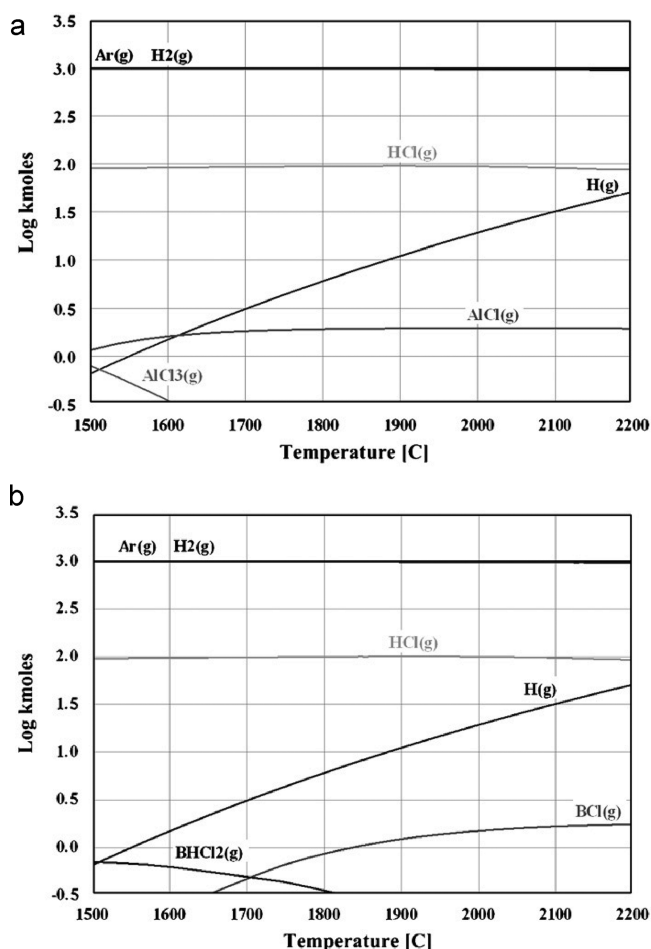
**3.6.2. N-Type Doping.** Intentional n-type doping has been investigated using the HCl approach for both nitrogen (Figure 9a) and phosphorus donors,<sup>152</sup> using a TCS process for a thin doped structure<sup>72</sup> and also with a low temperature process using chloromethane.<sup>94,153</sup> The incorporation of the donor atoms was influenced by the C/Si ratio in a similar manner as when using standard chemistry. It appeared, furthermore, that the Cl/Si ratio will enhance the incorporation of the nitrogen atoms into the grown layer, especially at very high growth rates;<sup>152</sup> less influence of the Cl/Si ratio was noticed for low growth rates and when phosphorus was used as n-type dopant. It is suggested that the cause for this behavior is that, at a high growth rate, the high supply of HCl enhances the formation of SiCl<sub>2</sub> molecules in the gas phase, giving rise to a more efficient supply of Si atoms to the growing surface. This in turn increases the number of new C sites available on this surface and, thus, allows an enhancement of the nitrogen incorporation in the layer. In this first study,<sup>152</sup> the influence of other growth parameters, such as temperature, pressure, and growth rate, was not investigated over a sufficiently large range to be able to make a convincing comparison with the standard nonchlorinated chemistry. With the low temperature process (below 1550 °C<sup>153</sup>), a complex dependency of the incorporation of the nitrogen was noticed for Si-face grown epitaxial layers with two regions; at very low temperature, the nitrogen incorporation decreased with increasing temperature, but in the 1450–1550 °C region, the nitrogen incorporation increased again. The difference in doping was almost 3 orders of magnitude when the temperature increased from 1450 to 1550 °C. This behavior is attributed to a severe change of the effective C/Si ratio on the growing surface due to changes in the carbon chemistry.



**Figure 9.** Dependence on the net doping as calculated from CV measurements for (a)  $N_2/\text{Si}$  ratio<sup>152</sup> and (b) Al/Si ratio<sup>157</sup> using the HCl approach with C/Si = 1 and Cl/Si = 3. The growth conditions were 1570 °C and 200 mbar. Reprinted with permission from refs 152 and 157. Copyright 2009 Elsevier B. V.

Nitrogen doping has also briefly been studied at high temperature (2000 °C) in the growth of SiC bulk crystals with the HCVD process using SiCl<sub>4</sub> and methane as precursors. No effects of various process parameters on the nitrogen incorporation were studied; however, nitrogen doping in the  $10^{19} \text{ cm}^{-3}$  range was achieved.<sup>154</sup>

**3.6.3. p-Type Doping.** Incorporation of acceptor atoms such as B, Al, and Ga (hereafter denoted III) has been investigated with a low temperature process using chloromethane,<sup>155,156</sup> at 1570 °C using the HCl approach,<sup>157</sup> and at high temperature (2000 °C) with the HCVD (halide CVD) bulk process using tetrachlorosilane and methane as precursors.<sup>158</sup> The formation of III–Cl<sub>x</sub> volatile species was proposed to limit the incorporation of the acceptor (III) into the SiC matrix. Thermodynamic calculations suggest that the monochlorides (III–Cl) are formed at higher temperatures and are also stable at very high temperatures (Figure 10). The stability of the monochlorides increases with increasing atomic number for the III-elements,<sup>159</sup> and in line with this, Ga was found to be very difficult to incorporate at 1570 °C<sup>157</sup> while the Al incorporation was found to be more limited than the B incorporation at high temperature growth.<sup>157,158</sup> As for the standard process without chlorine, the Al incorporation increases with increasing C/Si ratio and is higher in epitaxial layers grown on the Si-face compared to the C-face. However, saturation of the incorporation of Al atoms was



**Figure 10.** Gas phase species present at thermodynamic equilibrium in the (a) Si–C–H–Cl–Al and (b) Si–C–H–Cl–B systems. Reprinted with permission from ref 158. Copyright 2008 Elsevier B. V.

observed at a lower level than that obtained with the standard process without chlorine, typically  $10^{18} \text{ cm}^{-3}$  instead of  $10^{20} \text{ cm}^{-3}$  (Figure 9b). Less or no tendency was observed for the B atoms incorporation, for which a concentration in the  $10^{19} \text{ cm}^{-3}$  range was reported.<sup>157,158</sup> However, using the low temperature process ( $1300 \text{ }^\circ\text{C}$ ) with chloromethane as the carbon precursor, an Al atomic concentration in the  $10^{20} \text{ cm}^{-3}$  range, as measured by SIMS, has been reported together with a lower growth rate of  $1.5 \text{ } \mu\text{m/h}$ .<sup>155,156</sup> This behavior can be explained by an enhanced formation of the less stable  $\text{AlCl}_3$  species over the  $\text{AlCl}$  species, at the low growth temperature. Growth related defects generated at the highest p-type dopings at low temperatures have been studied and are suggested to be caused by precipitates, indicating that not all incorporated aluminum atoms are electrically active.<sup>160</sup>

**3.6.4. Deep Level Defects.** Intentional introduction of deep level defects for the growth of semi-insulating SiC epitaxial layers has been studied by chloride-based CVD thru intentional vanadium doping during the growth. By using  $\text{VCl}_4$  as vanadium source, V-doped semi-insulating epitaxial layers were grown using the  $\text{SiCl}_4 + \text{CH}_3\text{Cl}$  approach, both at standard growth rates ( $6 \text{ } \mu\text{m/h}$ ) at  $1450 \text{ }^\circ\text{C}$  and high growth rates ( $60 \text{ } \mu\text{m/h}$ ) at  $1600 \text{ }^\circ\text{C}$ .<sup>161</sup> Semi-insulating properties with resistivities in the  $10^5 \text{ } \Omega \text{ cm}$  range were observed for epitaxial layers grown under both process conditions. It was found that vanadium concentrations

up to  $1 \times 10^{17} \text{ cm}^{-3}$  could be incorporated in the SiC epitaxial layers without morphology deterioration.

Both optical and electrical techniques have been used to investigate the impurity incorporation in SiC epitaxial layers when using chloride-based CVD. The low temperature photoluminescence (LTPL) spectra at  $2 \text{ K}$  of as-grown epitaxial layers have been recorded in both the visible and infrared regions. The visible PL spectra are dominated by the near band gap emission. No luminescence from donor–acceptor pair recombination is observed. The rare observation of PL lines related to Ti impurity was associated with the degradation of the susceptor coating. The PL line related to the  $\text{D}_1$  center<sup>162</sup> was weakly observed; this shows that the results are comparable with those obtained from epitaxial layers grown using the standard chemistry without chlorine.<sup>163</sup> Hydrogen related lines have been observed from layers grown at very high growth rate (typically higher than  $120 \text{ } \mu\text{m/h}$ ) and when the conductivity of the layer was p-type. In the infrared region even when the epitaxial layer conductivity was shifted to p-type, no luminescence has been reported, to the best of our knowledge.

Electrical measurements have been carried out on Schottky diodes fabricated on epitaxial layers grown with the HCl approach, and very low leakage current was measured.<sup>37</sup> Deep level transient spectroscopy (DLTS) done on those diodes revealed a very low concentration, less than  $10^{13} \text{ cm}^{-3}$ , of deep traps. A reduction of the  $\text{EH}_{6,7}$  center<sup>164</sup> concentration with increasing Cl/Si ratio could be seen, and the surprising absence of the  $\text{Z}_{1/2}$  levels<sup>165</sup> for the highest Cl/Si ratio tried was also observed.<sup>166</sup> DLTS measurements were also reported from another group using HCl in the growth process;<sup>41</sup> however, the mentioned growth rate was only  $7 \text{ } \mu\text{m/h}$  at a temperature around  $1550 \text{ }^\circ\text{C}$ . The concentration of both the  $\text{Z}_{1/2}$  and  $\text{EH}_{6,7}$  levels was estimated to be less than  $8 \times 10^{11} \text{ cm}^{-3}$ , and the minority carrier lifetime was reported to be  $2\text{--}5 \text{ } \mu\text{s}$  for a  $38 \text{ } \mu\text{m}$  thick epitaxial layer.

The DLTS spectra of the epitaxial layer grown with MTS were dominated by the  $\text{Z}_{1/2}$  and  $\text{EH}_{6,7}$  features.<sup>163</sup> The concentration of those defects was dependent on the C/Si ratio, with a similar tendency as reported for epitaxial layers grown using the standard chemistry. Their concentrations were also slightly decreased when increasing the Cl/Si ratio. Typical concentrations were however in the mid  $10^{13} \text{ cm}^{-3}$  range, which is comparable to the highest range reported for nonchlorinated grown epitaxial layers. For growth rates higher than  $100 \text{ } \mu\text{m/h}$ , the  $\text{UT}_1$  defect<sup>167</sup> was observed, located at  $E_C = -1.39 \text{ eV}$  (note that this sample had n-type conductivity with a net carrier concentration of  $3 \times 10^{14} \text{ cm}^{-3}$ ). Using minority carrier transient spectroscopy (MCTS), the shallow and deep boron complexes were observed with concentrations in the low  $10^{13} \text{ cm}^{-3}$  range as well as the HS1 defect.<sup>168</sup> No additional, unidentified defects were reported.

#### 4. CHLORIDE-BASED GROWTH OF SILICON CARBIDE BULK CRYSTALS

Silicon carbide bulk crystals are normally grown using the physical vapor deposition (PVT) technique.<sup>169</sup> This technique is very simple; a source of SiC is sublimed in a crucible and the sublimed species are condensed onto a seed normally attached to the lid of the crucible. The encouraging growth rates obtained from the chlorinated epitaxial growth make it tempting to use the same technique for crystal growth. There have, however, only been two serious attempts at chlorinated crystal growth, to the

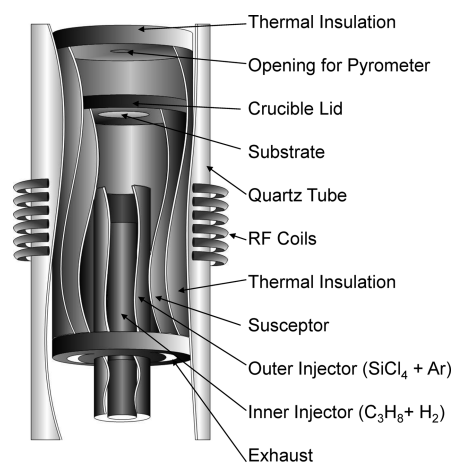
best of our knowledge. The first is the HCVD approach developed by Fanton et al. presented in 2004.<sup>170</sup> Their approach was to introduce  $\text{SiCl}_4$  and a hydrocarbon separately into the vertical growth chamber through a coaxial injector. The second report is by Leone et al. in 2010,<sup>171</sup> where the precursors are introduced together in a vertical reactor orientation.

There is one more bulk growth technique which merits mentioning; the continuous feed PVT technique.<sup>172</sup> This technique introduces the source through gases which are brought to react in porous foam. The material in the foam will sublime and then condense on a seed. Various gases have been used in this technique, including the chlorinated precursor MTS. Using MTS in hydrogen, they obtained a growth rate of  $35 \mu\text{m/h}$  at  $1900^\circ\text{C}$ . Increasing the temperature to  $2000^\circ\text{C}$  decreased the growth rate to zero.<sup>173</sup> Other precursors gave better results; however, as this technique is more characterized as a PVT technique, it will not be mentioned further in this review.

In the HCVD process, the  $\text{SiCl}_4$  is introduced in the outer part of the gas injector with an Ar carrier (Figure 11). The low thermal conductivity of the Ar shields the inner injector where the hydrocarbon flows with a hydrogen carrier. The  $\text{SiCl}_4$  is thermally stable and will not readily decompose in the inert Ar atmosphere; however, once the stream meets with the inner injector, then, in the presence of the hydrogen,  $\text{SiCl}_4$  will decompose and react with the hydrogen. Simulations show that there is very little reaction between the hydrocarbon and the chlorosilane species going on. The main species in the gas phase that are useful for the growth are  $\text{SiCl}_2$ ,  $\text{SiCl}$ , and  $\text{C}_2\text{H}_2$ .<sup>174,175</sup> The hydrocarbon plays an important role in the HCVD process. When propane was used, premature decomposition of propane took place which deposited as carbon on the injector walls or led to the formation of  $\text{C}_2\text{H}_2$  through the interaction of hydrogen. The hydrogen could also react with the graphite walls of the injector. At higher temperatures, the supply of  $\text{C}_2\text{H}_2$  into the growth chamber is determined solely by the flow of hydrogen and the temperature, which is a situation to avoid, since it leads to poor control of the C/Si ratio.<sup>176</sup> This was avoided by exchanging the propane with methane, which proved to be stable enough to prevent the premature reaction at the temperatures manifest in the inner injector.<sup>154</sup>

The growth process is carried out at low pressure (40–400 Torr) and at a seed temperature between 1800 and  $2150^\circ\text{C}$ .<sup>177</sup> The growth rate depends strongly on both the  $\text{SiCl}_4$  and the  $\text{CH}_4$  flows, which depend on whether the process is operating under Si-rich or C-rich conditions. However, the growth rate is very insensitive to the temperature, where only a slight decrease of the growth rate can be seen at higher temperatures. Typical growth rates obtained by the HCVD technique were in the range  $100\text{--}300 \mu\text{m/h}$ .<sup>176</sup> The process could be sustained for long periods of time, lasting for up to 30 h and yielding crystals up to 5 mm in length without clogging of injectors or the outlet. However, it has been reported that high growth rates were difficult to maintain for a prolonged period of time (more than 20 h), which is caused by a degradation of the insulating material causing drifts in the system. By reducing the amount of hydrogen in the system, the authors could increase the growth time to 30 h with less than 10% drift in the radiofrequency power.<sup>154</sup>

The material properties vary depending on the growth conditions. At higher C/Si ratios, the resistivity of the grown material was as high as  $10^{10} \Omega \text{ cm}$ , and at low C/Si ratios, the material exhibited n-type conduction with a nitrogen concentration in the  $10^{14} \text{ cm}^{-3}$  range. The electron mobility of crystals having a



**Figure 11.** Schematic drawing of the HCVD reaction chamber, showing the splitting of the Si and C precursor flows. Reprinted with permission from ref 176. Copyright 2006 Trans Tech Publications.

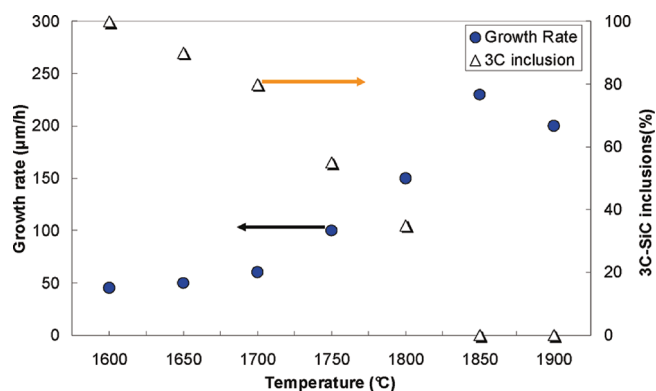
low n-type carrier concentration ranged between 220 and  $250 \text{ cm}^2/(\text{V s})$ .<sup>177</sup> Boron was also present in the material, though at low concentration, around  $10^{15} \text{ cm}^{-3}$ .<sup>178</sup>

The growth method proved to close micropipes very efficiently; about 90% of the micropipes closed, according to the authors.<sup>177</sup> In the same paper, a study of how the method behaved with respect to dislocations was also discussed. The method does not reduce the total amount of dislocations; however, the concentration of basal plane dislocations (BPDs) reduced by a factor of 20 for a  $200 \mu\text{m}$  thick layer. The BPDs convert into threading edge dislocations. X-ray rocking curve measurements on 6H-SiC material exhibited a FWHM which was as small as 19 arcsec, underlining the very high material quality produced by the method. The X-ray FWHM was categorically narrower for the grown material as compared to the seed.<sup>177</sup> Polytype stability is very good in the HCVD method as long as 6H is grown on the 6H Si-face and 4H is grown on the 4H C-face. 4H-SiC grown on the 4H Si-face showed some instability, and it is only for low growth rates ( $80 \mu\text{m/h}$ ) that the 4H polytype could be maintained. It is encouraging to note, however, that the 4H stability on the 4H Si-face is insensitive to the C/Si ratio, provided the growth rate is in the lower range.<sup>175,176</sup>

As mentioned above, both n- and p-type SiC crystals have been grown by the HCVD method and the dopants incorporation follows the site competition theory as for standard SiC CVD growth.<sup>154,158</sup> Also, semi-insulating 6H material has been grown at high C/Si ( $\text{C/Si} > 0.35$ ); the Fermi level was here found to be pinned by heavily compensated B acceptors.<sup>178</sup>

The C/Si ratios used in the HCVD process are low; often below 0.5. The usable C/Si range for various conditions has been identified through thermodynamical calculations, and a model to explain trends in growth rate and the occurrence of polycrystalline growth under certain growth conditions has been suggested and verified by experiments.<sup>179</sup>

Deep level electron and hole traps in the material grown by the HCVD technique have been studied by DLTS, MCTS, and thermal admittance spectroscopy (TAS). All traps found had previously been reported in CVD and PVT grown SiC. The trap concentrations were also found to decrease with increasing C/Si ratio.<sup>178,180</sup> Also, electron paramagnetic resonance (EPR) measurements have been done on highly resistive HCVD grown



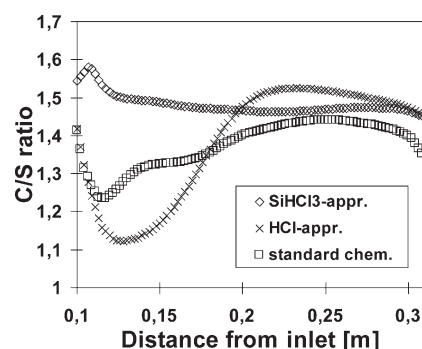
**Figure 12.** Growth rate and 3C-inclusions for different temperatures in the bulk growth process presented by Leone et al.; the C/Si and Cl/Si ratios were 0.5 and 10, respectively. Reprinted with permission from ref 171. Copyright 2010 American Chemical Society.

material, and both the carbon vacancy<sup>178</sup> and carbon vacancy carbon anti site pair<sup>181</sup> have been detected.

Another, perhaps less elegant, method for crystal growth with chloride-based chemistry, is presented by Leone et al.<sup>171</sup> This method uses the same conditions as in the horizontal epitaxial growth, *i.e.* with all the gases mixed in advance, but with a vertical orientation with the gas inlet at the bottom, similar to the HCVD system. The grounds for choosing such a system design were that the chloride-based CVD epitaxy process provided excellent material quality at very high growth rates yet at very low temperatures (1600 °C) and the vertical orientation would simplify the growth of crystals. In the study, a series of experiments were performed using SiH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and HCl at different temperatures. The hydrogen flow and pressure were 20 slm and 400 Torr, respectively. The process rendered polycrystalline 3C-SiC at 1600 °C, and as the temperature increased, the crystallinity improved and the amount of 3C inclusions reduced rapidly to completely vanish at a temperature of 1850 °C. Concurrently, the growth rate increased from about 50 μm/h at 1600 °C to about 250 μm/h at 1850 °C, where the growth rate was maximum (Figure 12). At higher temperatures, the etching from the HCl and hydrogen began to dominate, which will rapidly reduce the growth rate. Higher growth rates could however be obtained using SiCl<sub>4</sub>. The material quality was high, especially on on-axis or nearly on-axis substrates. The process typically closed all micropipes in the substrate, dissociating them into several screw dislocations. Basal plane dislocations converted into threading edge dislocations, as expected from a process that is technically a CVD process. The density of screw dislocations was high; this was explained by the high density of micropipes in the original substrates. Low temperature PL spectra of the layers showed sharp lines related to nitrogen bound excitons and free excitons, which is a further indication of the high quality of the material.

## 5. SIMULATIONS OF CHLORIDE-BASED SILICON CARBIDE CVD GROWTH

Simulation of the CVD process is one of the best ways to gain a deeper understanding of the chemistry in the process; it is also an essential tool for reactor development and reactor scale up. The standard, nonchlorinated SiC CVD process has been successfully modeled; see *e.g.* refs. 182–186, leading to an improved understanding of the growth process. Recently, a gas-phase and surface



**Figure 13.** Gas-phase C/Si ratio profile along the susceptor for the SiHCl<sub>3</sub> + C<sub>3</sub>H<sub>8</sub> process, the HCl approach, and the standard, nonchlorinated chemistry process. Process temperature is 1600 °C, and input C/Si = 1.5 and Si/H<sub>2</sub> = 0.017% for all cases and Cl/Si = 3 for the chlorinated processes.

reaction model for both Si- and C-terminated surfaces has been proposed.<sup>186</sup> By using this model, the CVD process can be discussed on the basis of the surface chemistry, rather than susceptor design and gas flow patterns. The modeling can then be used to predict growth rate, etching rate, surface morphology, and doping.

Simulations of chloride-based SiC CVD processes have mainly been focused on describing the differences in gas chemistry and growth rate, induced by the addition of chlorine. Numerical modeling has been done on chloride-based CVD with the HCl approach,<sup>187–189</sup> with the SiH<sub>x</sub>Cl<sub>y</sub> approach with SiHCl<sub>3</sub>,<sup>188,190–192</sup> and with SiCl<sub>4</sub> for bulk growth using HCVD described above<sup>174,175,193–197</sup> and for bulk growth using the HTCVD method,<sup>198</sup> and the CH<sub>x</sub>Cl<sub>y</sub> approach has been modeled for CH<sub>3</sub>Cl.<sup>191</sup> These reports show the clear difference in gas phase composition for the chloride-based CVD process as compared to the standard SiC CVD process; the most important Si species in the gas phase is SiCl<sub>2</sub> instead of SiH<sub>2</sub>. The SiCl<sub>2</sub> species is always formed,<sup>190,199</sup> no matter which chloride-based approach is used, and it is always the most important Si species for the growth.

A significant difference between the Cl-based and the standard process that has been demonstrated through calculations is the stability of the C/Si ratio in the gas phase over large areas.<sup>192</sup> The C/Si ratio in the gas phase obtained from the simulations, from close to the susceptor inlet ( $X = 0.1$  m) to the outlet ( $X = 0.3$  m) is plotted in Figure 13. The results for the standard process and the TCS process have previously been presented,<sup>192</sup> and data for the HCl approach<sup>200</sup> is now added to the plot. In the simulations, the inlet C/Si ratio is set to 1.5 for all cases, and the Cl/Si ratio is set to 3 for the cases with chlorine. By using the standard chemistry, the gas mixture must be transported approximately 0.25 m into the susceptor before the chemistry is set for the SiC growth with the intended C/Si ratio, while, with TCS as precursor, the chemistry is set already around 0.12 m into the susceptor. When using TCS, the C/Si ratio is also more stable through the susceptor, as compared to the standard nonchlorinated chemistry. This stability in the C/Si ratio is also manifest when the HCl approach is used; however, the gas mixture needs to be transported further into the susceptor, approximately 0.18 m, for the chemistry to be set. This is most likely due to the more complicated chemistry of the HCl approach, compared to the TCS approach. To form SiCl<sub>2</sub> from SiH<sub>4</sub> + HCl, six chemical bonds must be broken (four Si–H and two H–Cl bonds) and

two Si–Cl bonds must be formed; to form  $\text{SiCl}_2$  from TCS, only two bonds must be broken (one Si–H and one Si–Cl). These results strongly suggest that chloride-based CVD leads to a more stable process with higher uniformity in doping and that the chemistry of the various chloride-based approaches can significantly change the available growth area.

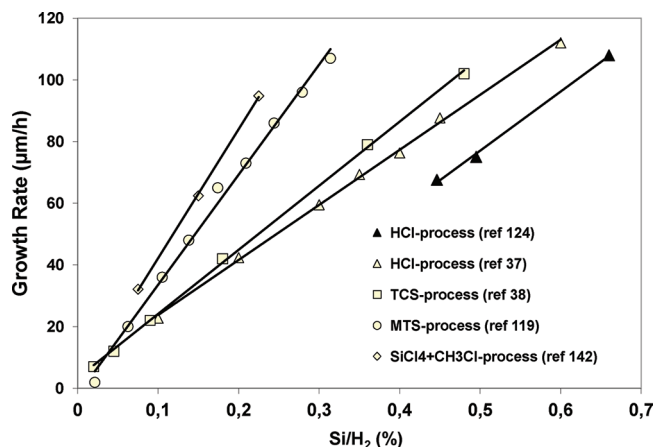
Currently, for simulation of chloride-based SiC CVD, each chloride-based approach needs specific gas phase and surface reaction models. There is no general model that can be used for various chloride-based systems. Newly developed models can still describe the chloride-based CVD process in terms of growth rate and surface morphology.<sup>201</sup> However, the simulation models still need improvement; this is particularly important for the industrialization of chloride-based SiC CVD.

## 6. COMPARISONS BETWEEN DIFFERENT CHLORINATED CHEMISTRIES

Although simulation is the most straightforward method to understand the details of the chloride-based growth process, simple comparisons between growth rates and process windows for different processes using the various approaches can bring valuable insight to the chemistry of the processes. Also, from an industrial point of view it is important to know which is the most efficient process in order to minimize the amount of unreacted precursors that may form deposits upstream of the substrate or downstream of the susceptor, which requires substantial cleaning of the system.

When studying the growth rates achieved for different molar fractions, using the different chloride-based approaches for a 100  $\mu\text{m}/\text{h}$  process, *i.e.* the HCl approach, the  $\text{SiHCl}_3$  approach, the MTS approach, and the  $\text{SiCl}_4 + \text{CH}_3\text{Cl}$  approach, one can note a difference in the amount of precursors needed to achieve a growth rate of 100  $\mu\text{m}/\text{h}$ . This comparison has been reported for the comparison between the HCl,  $\text{SiHCl}_3$ , and MTS approaches.<sup>124</sup> Now we can also add the  $\text{SiCl}_4 + \text{CH}_3\text{Cl}$  approach<sup>142</sup> to the comparison, presented in Figure 14, where the growth rates obtained on 8° off-axis 4H-SiC substrates are plotted against the silicon molar fraction for the various approaches, and linear trend lines are fitted to the data. Growth rate data for the  $\text{SiH}_2\text{Cl}_2 + \text{C}_3\text{H}_8$  process has not been added to the figure, since no data for the growth rate versus precursor concentration with a constant C/Si ratio has been presented.<sup>73</sup> Growth rates on the order of 100  $\mu\text{m}/\text{h}$  are achieved for all four precursor approaches; however, it can be seen that the linear slopes for the different chemistries are different, implying that the precursors are not equally efficient. Here it should be noted that the growths are done by different groups, in different laboratories, and in different reactors. The process parameters such as the C/Si and Cl/Si ratios used are also different for the different chemistries; however, the processes are optimized to give epitaxial layers with good morphology. The slope of the lines can be used as a measure of the efficiency of the process; a steeper slope means a more efficient process, and a shift between two parallel lines, such as the data from the two HCl processes, can be seen as differences in reactor optimization or differences in etching. The  $\text{SiCl}_4 + \text{CH}_3\text{Cl}$  and MTS processes need the lowest Si molar fraction, approximately only 0.2 and 0.3%, respectively, for a 100  $\mu\text{m}/\text{h}$  process. Comparatively trichlorosilane with ethylene needs a Si molar fraction of about 0.5%, and the HCl process requires a Si molar fraction of approximately 0.6%.

The most efficient processes according to Figure 14 are the three that use molecules with Si–Cl bonds, which should lead to

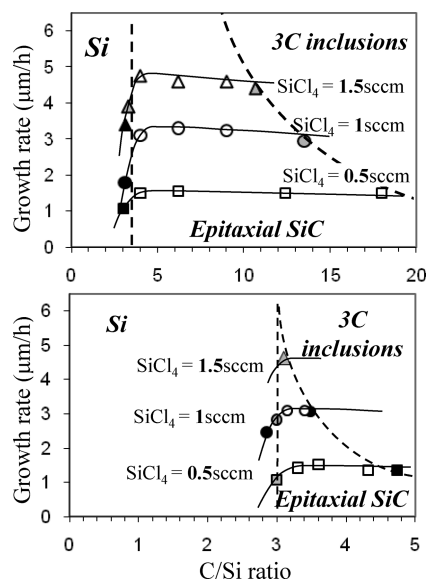


**Figure 14.** Plot of growth rates achieved for various silicon concentrations ( $\text{Si}/\text{H}_2$ ) using different chloride-based processes presented in refs 37, 38, 119, 124, and 142. The process conditions reported are as follows: 1600 °C and 133 mbar in refs 37 and 38, 1600 °C and 100 mbar in ref 119, 1570 °C and 200 mbar in ref 124, and 1600 °C and 187 mbar in ref 142. Linear trend lines have been fitted to data extracted from the references. A higher slope of the line indicates a more efficient growth process.

a significantly less complicated chemical path for the formation of  $\text{SiCl}_2$ , which, according to simulations, is the molecule that has been pointed out as the most important growth species. However, the MTS and  $\text{SiCl}_4 + \text{CH}_3\text{Cl}$  processes seem to be significantly more efficient than the TCS process with ethylene. This suggests that, although the chloride-based processes mainly change the silicon chemistry, also the carbon chemistry can be optimized. The decomposition of both the MTS and  $\text{CH}_3\text{Cl}$  molecules provides methyl groups ( $\text{CH}_3$ ) to the gas phase by breaking a single chemical bond; that is, the carbon chemistry is ready for the growth after breaking just one chemical bond. The TCS process uses  $\text{C}_2\text{H}_4$  as carbon source,<sup>38</sup> which decomposes (in several steps) mainly to  $\text{C}_2\text{H}_2$ ,<sup>191</sup> which has a lower sticking coefficient than  $\text{CH}_3$ ,<sup>202</sup> which would lead to a less efficient growth process.

The role of  $\text{CH}_3\text{Cl}$ , mainly in the low temperature process, has been described above. An improved growth mechanism has been noted, and the use of  $\text{CH}_3\text{Cl}$  as carbon precursor seems to improve the process beyond just supplying chlorine.<sup>68,146</sup> This was studied by comparing the  $\text{CH}_3\text{Cl}$  and  $\text{C}_3\text{H}_8$  precursors, while using  $\text{SiCl}_4$  as the silicon precursor. The main evidence of the superior properties of  $\text{CH}_3\text{Cl}$ , as compared to  $\text{C}_3\text{H}_8$ , was in the much wider operating window to obtain a growth process that did not degrade when the C/Si was varied (Figure 15). The lower C/Si boundary (the onset of Si condensed phase formation) was observed at roughly the same C/Si ratio for both carbon precursors. However, the transition to polytype inclusions and polycrystalline degradation took place at significantly higher values of the C/Si ratio when  $\text{CH}_3\text{Cl}$  was used instead of  $\text{C}_3\text{H}_8$ .

Furthermore, when the value of the Cl/Si ratio in the  $\text{C}_3\text{H}_8$  experiments was increased by adding HCl and even exceeded the Cl/Si ratio in the  $\text{CH}_3\text{Cl}$  growth without HCl by a few times, the C/Si window width in the  $\text{C}_3\text{H}_8$  growth remained more than 6 times narrower than that of  $\text{CH}_3\text{Cl}$  growth without HCl addition. Consequently, the role of  $\text{CH}_3\text{Cl}$  extends beyond serving as a source of Cl for suppressing homogeneous nucleation. However, the exact nature of the improvement remains unclear. It was noticed in ref 68 that the differences between the chlorocarbon and hydrocarbon growth could not be explained by simply using a



**Figure 15.** Comparisons of the process windows for the low temperature growth process using  $\text{CH}_3\text{Cl}$  (top) and  $\text{C}_3\text{H}_8$  (bottom) as carbon precursor; in both cases,  $\text{SiCl}_4$  was used as silicon precursor. Notice the differences in C/Si ratio in the figures. Reprinted with permission from ref 68. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

thermodynamic analysis of the stability of the condensed phase. Instead, it was suggested that the effect must be related to the surface reaction kinetics, different surface diffusivities, and different sticking coefficients of the dominating products of the chlorocarbon decomposition.

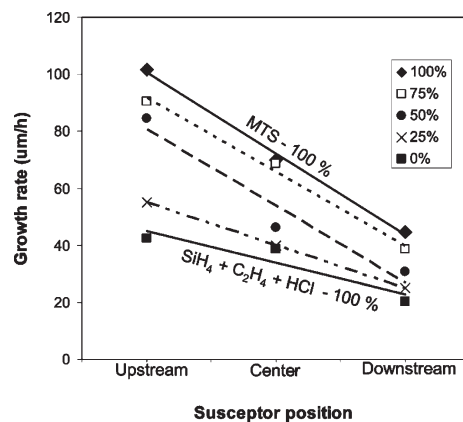
Thus, it seems that, by using  $\text{CH}_3\text{Cl}$  or MTS, the carbon chemistry becomes less complicated and contributes further to a more efficient process.

The higher efficiency for the MTS approach compared to the HCl approach has also been shown for growth on on-axis substrates,<sup>45</sup> where a growth process using pure MTS as precursor rendered twice as high growth rate as compared with a process using only HCl + silane + ethylene as precursors. It was further shown that, when mixing the two precursor approaches, the growth rate increases with increasing MTS content in the mixture (Figure 16). Also, at low growth temperature the MTS approach was found superior to the HCl approach:<sup>47</sup> Homoepitaxial growth of 4H-SiC at 1300 °C using MTS, with some addition of ethylene and HCl to adjust C/Si to 1.35 and Cl/Si to 15, demonstrated a growth rate of 13  $\mu\text{m}/\text{h}$ . The optimum C/Si and Cl/Si ratios for the HCl approach were found to be 0.75 and 10, respectively, which gave a growth rate of 7.5  $\mu\text{m}/\text{h}$ . It was suggested that the almost doubled growth rate achieved by the MTS approach was due to the different growth chemistry provided by the MTS molecule.

In bulk growth experiments at low temperature (1850 °C), the use of a chlorinated silane molecule has been shown to be superior to the use of silane plus HCl.<sup>171</sup> By replacing  $\text{SiH}_4 + \text{HCl}$  with  $\text{SiCl}_4$ , the growth rate increased from 250  $\mu\text{m}/\text{h}$  to 350  $\mu\text{m}/\text{h}$ , which was attributed to the higher efficiency of the chemistry provided by the chlorinated silane precursor.

## 7. GROWTH CONDITIONS FOR DIFFERENT OFF-AXIS SUBSTRATES

The epitaxial growth of 4H- and 6H-SiC is usually done on substrates having a defined off-angle toward the  $[11\bar{2}0]$  direction.



**Figure 16.** Plot of the growth on on-axis substrates vs position in the susceptor for the MTS and the HCl approaches and mixes of the approaches. Reprinted with permission from ref 45. Copyright 2010 American Chemical Society.

For 4H-SiC, 4° and 8° off-axis are usually used, while 6H-SiC uses 3.5° off-axis. The reason why substrates were cut with such a high off-angle is mainly to have a step-flow controlled growth mode. This was introduced by Matsunami et al.,<sup>203</sup> and it represented a major breakthrough in SiC technology, because it opened up the possibility to grow high quality epitaxial layers with perfect polytype replication at moderate temperatures (1500 °C).

There are two major drawbacks in basing the SiC technology on off-axis substrates: Bulk growth is an expensive process done on on-axis seeds; hence, the material waste when slicing a large crystal at high off-angles is too high, and basal plane dislocations propagate easily from the substrate to the epitaxial layer during epitaxial growth on off-angle substrates. Basal plane dislocations are recognized as a killer defect for bipolar devices and are hence crucial to eliminate. The SiC community is therefore striving toward low and preferably zero off angle substrates. In the case of 4H-SiC, 50 and 75 mm diameter wafers with the higher off-cut angle are marketed, but larger diameter wafers (100 mm) are available only with 4° and 0° off-axis.

Several studies have been done using the standard CVD process on different off-angles on 4H-SiC substrates in order either to reduce defect density for 8° off-axis<sup>204</sup> or to reduce surface roughness for 4° off-axis,<sup>205</sup> or for making homoepitaxial growth on on-axis substrates possible.<sup>206,207</sup> When using the standard, nonchlorinated chemistry, the growth rate is typically limited to around 10  $\mu\text{m}/\text{h}$ .

Since the introduction of the chloride-based CVD process, most research has been done on 8° off-axis substrates, as described in the previous sections of this review. The use of 4° off-axis wafers resulted in a very rough surface affected by step-bunching, unless the epitaxial layer thickness was limited to less than 40  $\mu\text{m}$ .<sup>70</sup> A study done under concentrated growth conditions (*i.e.* using a low carrier flow and pressure) on the three different off-axis orientations used for 4H-SiC<sup>46</sup> reveals that different growth conditions are required for different off-axis substrates. It does seem to be a general rule that the lower the off-angle, the more silicon rich conditions are required. This can be attained mainly by using a low C/Si ratio, but also in using a high Cl/Si ratio.

If no special *in situ* surface preparation is done prior to the growth, growth conditions for high quality epitaxial layers could look extreme; C/Si ratios as low as 0.3 and Cl/Si ratios as high as

30 have been reported for on-axis growth.<sup>44</sup> For 4° off-axis substrates, large triangular defects are the main problem. These may be reduced by using a low C/Si ratio (about 0.6) and Cl/Si ratios between 3 and 6.<sup>42</sup> As a comparison, for 8° off-axis wafers, a C/Si ratio of around 1 and a Cl/Si ratio of 1–3 are used.<sup>118,37</sup>

Chloride-based chemistry is also advantageous to use in reducing the density of epitaxial defects originating from dislocation sites.<sup>30</sup> A HCl *in situ* etching prior to the growth was demonstrated to be beneficial for 8° off-axis substrates,<sup>29</sup> but especially in the case of 4° off-axis substrates<sup>43</sup> when the growth temperature is kept low. In the case of on-axis substrates, a different surface preparation method based on silicon-rich conditions is required,<sup>125,126</sup> which eliminates the need for very silicon-rich conditions. If proper *in situ* etching prior to the growth is done, ratios similar to the ones used for 8° off-axis substrates could be employed even for on-axis substrates. In this way, growth rates of 100  $\mu\text{m}/\text{h}$  have been demonstrated for both 4° off-axis<sup>43</sup> and on-axis substrates.<sup>45</sup>

## 8. CONCLUDING REMARKS AND FUTURE OUTLOOK

From the above reviewed results on chloride-based growth of SiC, the following conclusions can be drawn:

- Several approaches can be used to provide chlorine to the gas mixture. The most straightforward approach is simply to add HCl to the standard chemistry, but chlorinated silane and hydrocarbon molecules can be used instead of, or together with, the standard chemicals (silane and light hydrocarbons). Single molecule approaches such as methyltrichlorosilane can also be used, although with the disadvantage of a fixed C/Si ratio. With the chloride-based chemistry, the Cl/Si ratio is introduced as a new process parameter; this ratio is important to fully describe the process. An extra source of chlorine, *e.g.* in the form of HCl, is often most useful for many processes. Very high growth rates, *i.e.* 100  $\mu\text{m}/\text{h}$  or higher, can be achieved using any of the chemical approaches.
- The use of chlorinated chemistry enables a growth process for SiC epitaxial layers by low temperature processes as low as 1300 °C with growth rates of approximately 5  $\mu\text{m}/\text{h}$ . Lower growth temperature results in substantially reduced wear of hot zone consumables, such as high purity graphite. This opens up new ways to more cost efficient and reproducible processes for SiC structures that do not require too thick epitaxial layers.
- For growth of electronic device structures, the essential n- and p-type doping can be controlled by using the C/Si ratio in the gas mixture in the same manner as in the standard, nonchlorinated chemistry growth. However, high p-type doping could be problematic to achieve with aluminum at high growth rate in chlorinated processes. The Cl/Si ratio can be used to control the amount of incorporated dopants.
- To the best of our knowledge, no new, unidentified deep level defects are shown to be formed due to the addition of chlorine to the process. Furthermore, the concentrations of deep level defects are similar to those normally found in SiC epitaxial layers grown using the standard, nonchlorinated chemistry.
- The use of chlorinated chemistry can potentially lead to new CVD-based processes for the growth of SiC bulk crystals. These processes would have the major advantage over today's PVT processes in that the starting material would

be gases which are available at very high purity, and very pure crystals could thus be grown. Moreover, these processes would likely have a process temperature of less than 2000 °C, which would reduce production costs due to the prolonged lifetime of graphite consumables in the reactor and lower power consumption; this could result in less expensive SiC substrates.

- Simulations show that the chlorinated process exhibits a particularly high degree of stability in the effective C/Si ratio over a wide area. Doping uniformity will be superior and easier to achieve when the process is scaled. This fact motivates the use of a chlorinated process also for thinner epitaxial layers where a high growth rate is less called for, and a higher yield from the process then can be expected.
- It is also clear that there are differences in the efficiency of the various chemical approaches that could be used. The highest potential for optimization seems to be for the silicon chemistry—by the use of a precursor with Si–Cl bonds, the most efficient processes are achieved. However, there is room for improvement by also working on the carbon chemistry: The use of carbon precursors that supply the process with single CH<sub>3</sub> groups is more efficient than processes using standard hydrocarbons.
- The chlorinated chemistry can be used for very high growth rate processes (100  $\mu\text{m}/\text{h}$  or higher) on any type of off-cut angle substrates. The major part of the research has been conducted on high off-cut angles, where the homopolytypic growth is very stable due to the high density of growth steps. But very high growth rates have also been demonstrated on on-axis substrates, which will likely be the substrate of choice for the SiC industry in the future.

The results reviewed in this paper show that chloride-based growth of SiC for electronic applications is not just a promising way to grow SiC, but it is most likely the future way to grow SiC. The technology is now ready to leave the research laboratories and move into the industrial fabs. Most likely an important step for industrialization will be the demonstration that the chloride-based processes can be implemented in large scale reactors and used for production of SiC device structures. Skeptical voices sometimes raise questions on what effect the addition of chlorine will have on the growth equipment used. One must then not forget that often for the SiC community it is the silicon industry that leads the way and the growth of silicon epitaxial layers has been done using chloride-based chemistry for several decades. In light of the silicon industry, the switch to chloride-based chemistry for the growth of SiC is logical. It is also possible that a switch to chloride-based chemistry will bring a revolution to the SiC growth equipment allowing the development of new types of CVD reactor solutions similar to the ones used for, *e.g.*, single wafer reactors for silicon epitaxial layers.

So why has not the chloride-based CVD growth become standard practice in the SiC industry? It is important to remember that the industry has an inertia toward changes that involve costly investments although these investments lead to a better process and/or higher quality of the material produced. As an example, the hot-wall CVD concept for SiC was introduced in 1993,<sup>208</sup> but it took several years for the industry to adopt it and today it is the standard technique for growth of thick SiC epitaxial layers. The studies on very high growth rate of SiC through addition of chlorine were reported in 2005, and now six years later, it is the signal from the SiC industry that chloride-based processes are being used for epitaxial growth.<sup>209</sup> However, the

growth of SiC bulk crystals is today mainly done by sublimation, and it is to a great extent developed by the companies in the SiC industry. Thus, it is very hard to know the level of understanding that exists today for this highly complex process. The conversion to chloride-based bulk growth is therefore likely to be further in the future, and significant research is still needed for commercialization of chloride-based bulk growth.

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Henrik Pedersen received his M.Sc. in Chemistry 2004 and his Ph.D. in Materials Science 2008 from Linköping University. His thesis topic was chloride-based CVD growth of SiC epitaxial layers. After one and a half years as a research engineer at Sandvik Tooling in Stockholm, where he did research and development of hard CVD coatings for cutting tools, he was recruited back to Linköping University, where he now holds a position as an assistant professor. His research interests include thermal- and plasma-CVD processes for functional materials such as SiC, BN, BC<sub>x</sub>, and amorphous carbon.



Stefano Leone studied Industrial Chemistry at the University of Catania (Italy), where he received his M.Sc. degree (magna cum laude) in 2002. He has been employed by companies such as LPE (Italy) and Caracal (USA) as a process engineer; he has worked with the development of new epitaxial reactors, with epitaxial and bulk growth of SiC, and with characterization.

He received his Ph.D. in Semiconductor Materials from Linköping University (Sweden) in 2010. He has been pioneering the chloride-based chemical-vapor-deposition of SiC since 2004, accumulating broad experience on the topic. He is author and coauthor of more than 40 papers related to SiC. He has since September 2011 been a research engineer at Aixtron in Aachen, Germany.



Olof Kordina received his Ph.D. at Linköping University in 1994. His thesis work was on epitaxial growth and characterization of SiC. He has been employed by several leading companies in the field: ABB, Cree Inc., Sterling Semiconductor (now Dow Corning), and Caracal Inc. He is now working at Linköping University as Associate Professor. Dr. Kordina is the inventor or coinventor of several important growth techniques. Among these can be mentioned the hot-wall concept for SiC epitaxial growth and the HTCVD concept for crystal growth of SiC. He has more than 100 publications and between 20 and 30 patents or patent applications.



Anne Henry received her Ph.D. degree in Physics, option Microelectronic, at Grenoble, France, in 1986. After a Post Doc (1987–1989) at Linköping University (LiU), she was employed as research assistant at the same place. During 6 years (1996–2002) she has also been employed by industries (ABB and Okmetic) and part time by LiU. Today she is a professor at LiU. Her research contribution is described in 100 journal articles, 200 conference contributions, and 5 book chapters. She has from the start of the SiC activities at LiU, 1992, been responsible for the characterization of SiC by photoluminescence. Since 1996, she has been responsible for the SiC epitaxial growth. She has also been involved in nitride



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Shin-ichi Nishizawa received his B.Eng. in 1989, M.Eng. in 1991, and Dr.Eng. in 1994 in Chemical Engineering from Waseda University. Then he worked at Waseda University as a research associate, where he carried out studies on transport phenomena with interfacial tension gradient driven flow under microgravity conditions. In 1996, he joined the space technology group of the Electrotechnical Laboratory (the former AIST) to work on crystal growth under microgravity. Since 1998, he has worked on SiC bulk crystal growth and epitaxy. From 2000 to 2002, he was the group leader of SiC bulk crystal growth, NSS project supported by METI, Japan. In 2006, he joined the group of Prof. Erik Janzen, Linköping University, as visiting professor. Since 2009, he has been the leader of the energy enabling technology group, energy technology research institute of AIST. He is a member of the Japan Society of Applied Physics, the Japanese Association for Crystal Growth. His research interests include semiconductor wafer technologies for power devices, such as Si, SiC, and diamond. More recently, his interests have been enlarged to green electronics for low carbonated and a sustainable society. He is the author and coauthor of over 70 publications and 10 patent publications.



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Erik Janzén received his Ph.D. in Solid State Physics in 1981 from Lund University, Sweden. He joined the company ABB in Västerås, Sweden, in 1983, working with fiber optic sensors and power devices. In 1989 he joined Linköping University but had between 1989 and 2001 also different part time positions at ABB and Okmetic. He has been since 1995 professor at Linköping University and since 2009 head of Semiconductor Materials. He has since the start of 1991 been the head of SiC research at LiU, which includes growth, characterization, and defect physics. He has led the early developments of the hot-wall SiC CVD reactor for epitaxial growth and the SiC HTCVD reactor for bulk growth. Since a few years ago, he has transferred the hot-wall technology also to the MOCVD growth of III-nitrides. He is author/coauthor of more than 500 publications, review articles, book chapters, and patents.

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