

Silicon carbide growth mechanisms from SiH_4 , SiHCl_3 and nC_3H_8

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A detailed chemical mechanism for the silicon carbide epitaxial growth using chlorinated precursors is presented here. The mechanism involves 155 gas phase and 66 surface reactions among 47 gas phase and 9 surface species, respectively. A comparison with the performances of the standard process using silane is presented and the observed growth rate increase and the disappearing of the homogeneous silicon droplets in gas phase is explained.

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1 Introduction

Although silicon will dominate microelectronics for the nearest future many important applications are limited by its properties. Therefore, wide band gap materials, such as silicon carbide and III-nitrides, hold properties that make them more attractive than silicon for high power, high frequencies and high temperatures devices. Particularly, the interest related to SiC growth is due to the presence on the market of substrates of ever increasing diameter. However, their quality is still not satisfactory for the above mentioned applications and thus the deposition of a high quality epitaxial layer is required. Unfortunately, also that last step is not easy to obtain and many problems still affect the present processes. High homoepitaxial growth is generally performed at reduced pressure (0.1–0.2 atm), high temperature (1800–1900 K) on off-axis SiC(0001) wafers owing the concept of step controlled epitaxy by Chemical Vapor Deposition. Those processes usually adopt SiH_4 and C_3H_8 diluted in H_2 acting as carrier gas. Moreover, N_2 and $\text{Al}(\text{CH}_3)_3$ or B_2H_6 precursors are used for the n- and p-type doping, respectively. Main challenges for this high temperature CVD processes are principally the control of the temperature and reactant concentration fields to improve the area meeting the industrial uniformity on performance parameters. On the other hand, one of the main problems that afflict the silane-propane system is the homogeneous gas phase nucleation, where solid/liquid particulates are formed in the gas phase. This phenomenon causes the depletion of the gas phase precursors available for the deposition (with a consequent reduction of the growth rate) and the worsening of the surface quality, due to the particulate impinging on the deposition surface. To remove such problems the use of chlorinated silicon precursors or simply the HCl addition was suggested in the literature and several processes of that kind are under development [1,2]. Unfortunately, information about the chemical mechanism involved in the deposition are lacking and thus the development of a new kinetic mechanism involving chlorine species is the aim of the present work. Due to its preliminary nature, at this stage only the system SiHCl_3 , H_2 , n- C_3H_8 will be examined, but the proposed mechanism can be easily extended also to the other most used chlorinated silicon precursors and to the HCl addition to not chlorinated ones. In fact, it is well known, that the most important gas phase species SiCl_2 is produced by all chlorosilanes and by SiH_4/HCl systems [3,4].

2 Reactor modeling

Silicon carbide films are usually grown in horizontal hot wall reactors with rotating susceptor operating at reduced pressure (0.1–0.2 atm) and high temperature (1500–1800°C). The fluid dynamics of these reactors was well investigated so far [5,6] and substantially laminar fully developed flow in the deposition region is

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evidenced. Thus, because our aim was the development of the detailed chemical mechanism involved in the growth, a simple 1D model based on the boundary layer approximation to describe the fluxes toward the deposition surface was adopted here [7,8]. It includes the materials balances for any involved species and for the whole system and the energy balance for the gas stream and due to its simplicity, it allows a fast investigation of all the kinetic aspects also when adopting complex kinetic schemes.

3 Chemical kinetics aspects

Silicon carbide epitaxy is usually conducted using silane as silicon precursor. Unfortunately, its use limits the process beyond the high dilution – low growth rate conditions to avoid the particulate (mainly liquid silicon drops) formation. Nowadays that is the limiting factor to achieve a satisfactory growth rate value. In this work the possibility to replace the silicon precursor with chlorosilanes, particularly SiHCl_3 , was analyzed. In that system, because its chemical complexity, the knowledge of a detailed gas phase mechanism is indeed of fundamental importance. During the last years many efforts were devoted to the study and comprehension of the chemical reactions involved in silicon carbide deposition mainly considering the $\text{SiH}_4/\text{C}_3\text{H}_8/\text{H}_2$ system and comprehensive mechanisms were proposed [5,9,10]. The simple replacement of SiH_4 with SiHCl_3 produces a significant alteration of the species involved whose key factor is represented by the shift from Si to SiCl_2 as the most important silicon gas phase species. While the former is the main responsible of the hazing phenomena, the latter is very stable and thus remain available to contribute to the film growth. Moreover, the HCl generated by SiHCl_3 decomposition contributes to the etching of surface spots, leading thus to surfaces of greater quality. Accordingly, the understanding of the above mentioned points is the main goal of this work.

Initially, an examination of the most stable species present at thermodynamics equilibrium conditions was done for both the systems (e.g., the SiH_4 and the SiHCl_3 ones). The simulation was performed by means of the Cantera software [11]. As it can be seen from the two graphs reported below in Figure 1 the main differences regarded the silicon-based species.

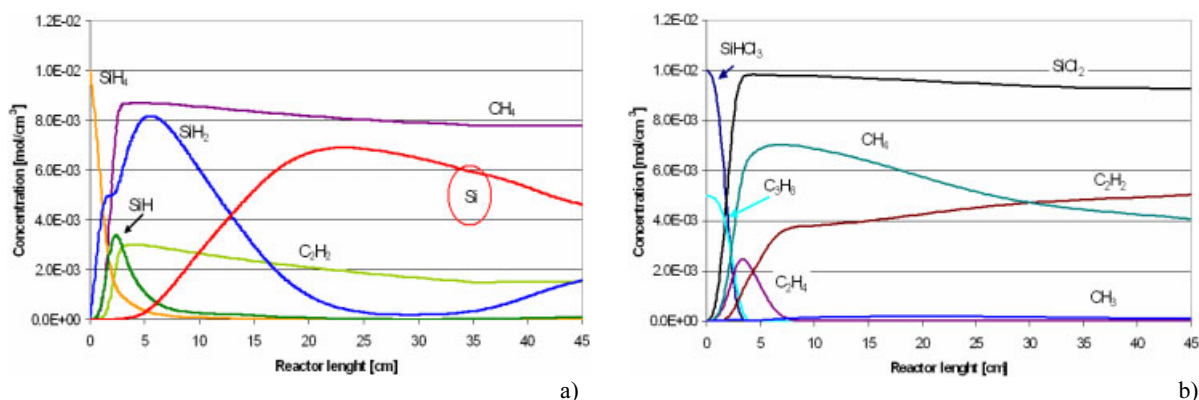


Fig. 1 Comparison between the main species at the equilibrium for the two reactive mixtures: (a) silane and (b) trichlorosilane precursor. C/Si = 1.5

In the case of silane the most abundant species were Si, SiH_2 and SiH . Being the atomic silicon in great amount along the reactor there was the possibility of homogeneous droplets nucleation. However, it is possible to check the upper limit of SiH_4 inlet concentration that avoid such phenomenon by simply matching the calculated silicon partial pressure inside the reactor with its vapor pressure. As it can be noted from Figure 2, where the maximum Si partial pressure inside the reactor, for different inlet silane molar fractions, is compared with its vapor pressure as a function of process temperature, it always exists a region where the Si partial pressure in gas phase is lower than the vapor pressure of the liquid Si and consequently hazing phenomena are not present. However, not always such a region is compatible with the industrially desired growth rates. In the temperature interval of interest for the SiC epitaxial deposition it can be concluded that an inlet silane mole fraction below $4 \cdot 10^{-4}$ should preserve the haze phenomenon.

As second step, a comparison between the composition profiles within the reactor in realistic growth conditions was performed. While the chemical mechanism embedded in the reactor model for the silane based system can be considered almost consolidated (at least for the gas phase reactions) a fully new one was here

developed for the trichlorosilane based system. That mechanism was derived by the previous one by linking it with the consolidated SiHCl_3 mechanism usually adopted for epitaxial silicon deposition [3,4]. Accordingly, its main pathways leading to the formation of the reactive and adsorbed species are illustrated in Figure 3. By its inspection, it can be seen that the dissociation of the precursors lead to almost the same carbon containing species of ref. [5], being the greater changes on the silicon side. Atomic silicon was still considered but its presence now is no longer important because the most abundant species was SiCl_2 . About the surface part of the mechanism, SiCl_2 adsorbs on the surface to produce the Si radicals that promote the growth. Moreover, in the mechanism the desorption of Si, SiCl_2 , HCl , H_2 was introduced.

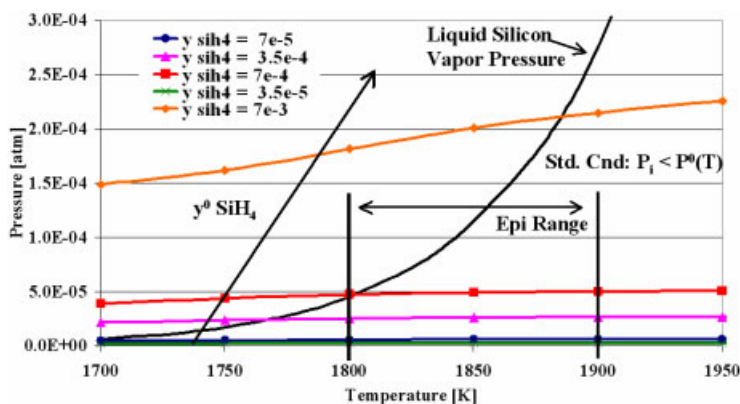


Fig. 2 Comparison between the maximum Silicon partial pressure within the reactor and its vapor pressure reported as a function of the temperature.

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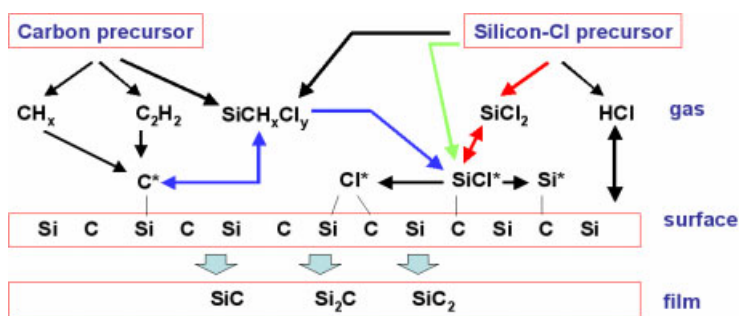


Fig. 3 Sketch of the main reaction pathways involved in the deposition mechanism (silicon species adsorbed on surface carbon and vice versa).

In conclusion the developed mechanism is formed by the merging of a traditional hydrocarbon/silane/hydrogen mechanism with the pyrolysis mechanism of chlorosilanes. Obviously redundant or unlikely reactions were removed in that process. About the surface reactions, the mechanism was derived again on the framework of the three fictitious solid species (SiC , Si_2C and SiC_2) that mimic the formation of stoichiometric, silicon rich and carbon rich lattices, respectively [5,6]. For space reasons, here only the rate constants for the main reactions inherent the silicon species involved in the mechanism described above are summarized in Table 1, because the other reactions can be found elsewhere [5,6].

Finally, a comparison between the growth rate profile along the reactor obtained with the two different precursors is reported in figure 4. The simulations were performed with reference to the reactor described in

ref. [5], with an inlet C/Si ratio equal to 1.5, a reactor temperature of 1550°C and a pressure of 0.1 atm, with a gas residence time of 0.2 s. The simulations were repeated for different inlet mole fraction for the silicon precursors to stress the process possibilities. By the inspection of the figure, it can be noted that the use of trichlorosilane leads to a great enhance in the growth rate avoiding the particulates formation in the gas phase. Moreover, the positive aspects are reflected also by the surface quality increases [1], because the quality of the surface today strongly depends on the impinging of the gas phase nucleated liquid droplets.

Table 1 Rate constants of main Si reactions involved in the SiHCl_3 , nC_3H_8 , H_2 system for epitaxial SiC growth (\$1 and \$2 Si and C surface sites, * adsorbed species, *S chlorine adsorbed on silicon sites and *C chlorine adsorbed on carbon sites). Rate constant: $k = AT^b e^{-E/RT}$, with parameters coherent with rates in $\text{mol}/\text{cm}^2/\text{s}$, gas and surface concentrations in mol/cm^3 and mol/cm^2 , activation energy in cal/mol .

	Gas Phase Reactions	Log ₁₀ A	b	E _a		Gas Phase Reactions	Log ₁₀ A	b	E _a
G-1	$\text{SiH}_3\text{Cl} = \text{HCl} + \text{SiH}_2$	14.69	0	75500	G-10	$\text{SiH}_2\text{Cl}_2 = \text{SiCl}_2 + \text{H}_2$	13.92	0	77386
G-2	$\text{SiH}_3\text{Cl} = \text{H}_2 + \text{SiHCl}$	14.59	0	65000	G-11	$\text{SiH}_2\text{Cl}_2 = \text{SiHCl} + \text{HCl}$	14.84	0	75786
G-3	$\text{SiH}_2\text{Cl}_2 = \text{SiHCl} + \text{HCl}$	14.81	0	73700	G-12	$\text{SiCl}_4 = \text{Cl} + \text{SiCl}_3$	15.68	0	111159
G-4	$\text{Si} + \text{HCl} = \text{SiCl} + \text{H}$	-8.8	0	13810	G-13	$\text{SiHCl}_3 + \text{H} = \text{SiCl}_3 + \text{H}_2$	12.39	0	2532
G-5	$\text{SiCl} + \text{HCl} = \text{SiCl}_2 + \text{H}$	-9.97	0	19490	G-14	$\text{HCl} = \text{H} + \text{Cl}$	13.64	0	81733
G-6	$\text{SiH}_2 + 2\text{HCl} = \text{SiCl}_2 + 2\text{H}_2$	14.97	0	19490	G-15	$\text{SiCl}_4 + \text{H}_2 = 2\text{HCl} + \text{SiCl}_2$	17.88	-0.87	22977
G-7	$\text{Si} + \text{HCl} = \text{SiHCl}$	11.62	0.5	0	G-16	$\text{SiHCl} + \text{HCl} = \text{SiCl}_2 + \text{H}_2$	11.62	0.5	0
G-8	$\text{Si} + \text{H}_2 = \text{SiH}_2$	12.08	0.5	0	G-17	$\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$	13.68	0	5258
G-9	$\text{SHCl}_3 = \text{SiCl}_2 + \text{HCl}$	14.69	0	73684					

	Chlorine Species Surface Reactions	Log ₁₀ A	b	E _a
A1	$\text{SiHCl}_3 + 2\$1 + 2\$2 = \text{SiCl}^* + \text{H}^* + 2\text{Cl}^*\text{S}$	16.42	0.5	0
A2	$\text{SiHCl}_3 + \$1 + 3\$2 = \text{SiCl}^* + \text{H}^* + \text{Cl}^*\text{S} + \text{Cl}^*\text{C}$	16.42	0.5	0
A3	$\text{SiH}_2\text{Cl}_2 + 2\$1 + 2\$2 = \text{SiCl}^* + 2\text{H}^* + \text{Cl}^*\text{S}$	8.58	0.5	0
A4	$\text{SiCl}_4 + 2\$1 + 2\$2 = \text{SiCl}^* + \text{Cl}^*\text{C} + 2\text{Cl}^*\text{S}$	16.37	0.5	0
A5	$\text{SiCl}_2 + 2\$2 = \text{SiCl}^* + \text{Cl}^*\text{C}$	19.49	0.5	0
A6	$\text{SiCl}_2 + \$2 + \$1 = \text{SiCl}^* + \text{Cl}^*\text{S}$	19.49	0.5	0
A7	$\text{HCl} + \$1 + \$2 = \text{CH}^* + \text{Cl}^*\text{S}$	10.55	0.5	0
A8	$\text{SiCl}^* + 0.5\text{H}_2 = \text{Si}^* + \text{HCl}$	12.37	0.5	60000
A9	$\text{SiCl}^* + \text{H} = \text{Si}^* + \text{HCl}$	12.52	0.5	60000
A-10	$\text{SiCl}^* + \text{HCl} = \text{SiCl}_2 + \text{H} + \2	10.55	0.5	0
A-11	$\text{SiCl}^* + \text{Cl}^*\text{C} = \text{SiCl}_2 + 2\2	23	0	20095
A-12	$\text{SiCl}^* + \text{Cl}^*\text{S} = \text{SiCl}_2 + \$1 + \$2$	23	0	89806
A-13	$2\text{SiCl}^* = \text{SiCl}_2 + \text{Si}^* + \2	23	0	89806
A-14	$\text{SiCl}^* + \text{CH}^* = \text{SiC} + \$1 + \$2 + \text{H}_2$	17	0	0
A-15	$\text{H}^* + \text{SiCl}^* = \text{HCl} + \text{Si}^* + \2	23	0	70006
A-16	$2\text{Cl}^*\text{C} + \text{H}_2 = 2\text{HCl} + 2\2	12.37	0.5	78580
A-17	$\text{Cl}^*\text{C} + \text{H} = \text{HCl} + 2\2	12.5	0.5	0
A-18	$2\text{Cl}^*\text{C} + \text{SiCl}_2 = \text{SiCl}_4 + 2\2	11.51	0.5	25000
A-19	$2\text{Cl}^*\text{S} + \text{H}_2 = 2\text{HCl} + 2\2	12.37	0.5	89806
A-20	$\text{Cl}^*\text{S} + \text{H} = \text{HCl} + \1	12.5	0.5	0
A-21	$\text{Cl}^*\text{S} + \text{Cl}^*\text{C} + \text{H}_2 = 2\text{HCl} + \$2 + \$1$	12.37	0.5	84190
A-22	$\text{Cl}^*\text{S} + \text{Cl}^*\text{C} + \text{SiCl}_2 = \text{SiCl}_4 + \$2 + \$1$	10.51	0.5	25000
A-23	$\text{CH}^* + \text{Cl}^*\text{S} = \text{HCl} + \text{C}^* + \1	23	0	89806
A-24	$\text{Si}^* + \text{Cl}^*\text{S} = \text{SiCl}^* + \1	17	0	0
A-25	$\text{H}^* + \text{Cl}^*\text{S} = \text{HCl} + \$2 + \$1$	23	0	89806
A-26	$\text{CH}^* + \text{Cl}^*\text{C} = \text{HCl} + \text{C}^* + \2	23	0	84190
A-27	$\text{Si}^* + \text{Cl}^*\text{C} = \text{SiCl}^* + \2	17	0	0
A-28	$\text{H}^* + \text{Cl}^*\text{C} = \text{HCl} + 2\2	23	0	84190
A-29	$\text{H}^* + \text{H}^* = \text{H}_2 + 2\2	23	0	61000
A-30	$\text{HCl} + \text{SiC} = \text{SiCl}^* + \text{CH}^*$	10.55	0.5	0

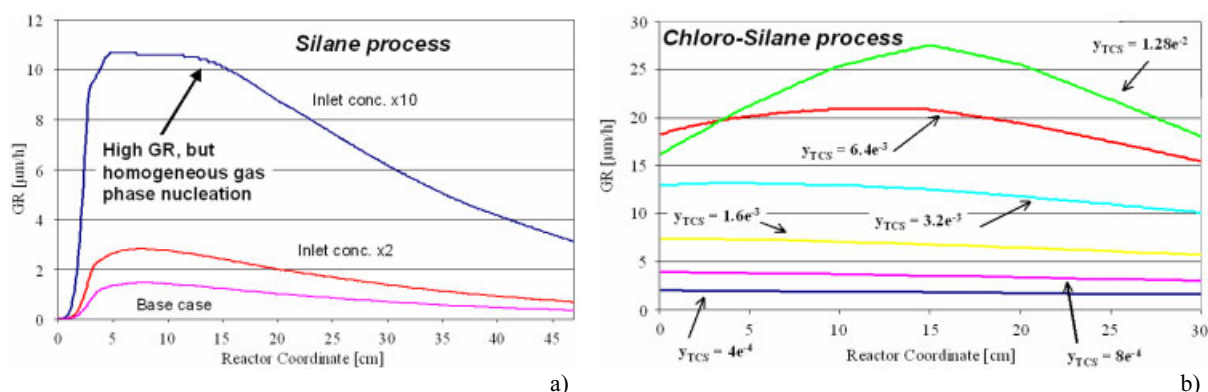


Fig. 4 Comparison between the growth rate profile along the reactor with (a) silane and (b) trichlorosilane.

4 Conclusions

In this preliminary work the development of a new kinetic mechanism regarding the Silicon Carbide Chemical Vapor Deposition using trichlorosilane instead silane as silicon precursor was performed. The developed mechanism was found consistent with the experimentally observed disappearing of the silicon homogeneous gas phase nucleation even at high precursor concentration and thus the possibility to obtain higher growth rate values with respect to the “traditional” process using silane. The whole mechanism is now under a generalization procedure to include the whole chlorosilanes system and also the SiH_4/HCl one.

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