Growth of Crystalline Silicon Carbide by CVD Using Chlorosilane Gases

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ABSTRACT

The forefront of semiconductor silicon carbide technology now approaches commercialization for both materials and device technology. The commercialization of SiC epitaxy processes requires improvement in defect density, uniformity and repeatability. Especially problematic are graphite particles, gas phase nucleation of particles and the limitations placed on achieving growth rates that can positively impact process costs. When it approached the same historical point of development, silicon epitaxy technology shifted to the use of chlorosilane precursor gases to suppress gas phase nucleation and achieve targeted growth rates. Recent work on SiC epitaxy chemistry now investigates the use of HCl, halocarbons and most recently chlorosilane precursors. This paper will review the original work on gas phase nucleation and its control in silicon epitaxy processes using HCl additives and chlorosilanes. Using established dissociation pathways for chlorosilanes, equilibrium chemical reaction models are used to assess the impact of HCl, halocarbons and chlorosilane precursors on growth rates and particle formation SiC epitaxy. Experimental data is presented on the comparative performance of HCl additive and chlorosilane precursors in SiC epitaxy and film properties.

INTRODUCTION

Chemical vapor deposition (CVD) technology used in silicon carbide epitaxy for semiconductor device applications historically teaches using hydrogen, monosilane (SiH₄) and hydrocarbon (C_xH_y) chemistry. This is an interesting contrast to the use of chlorosilane (H₄₋ _xSiCl_x) chemistry established in mass production silicon epitaxy processes for integrated circuit fabrication [1] and also the organo-chlorosilane ((CH₃)_ySiCl_x) chemistry often used in high temperature CVD processes for high temperature SiC coating on monolithic graphite. Semiconductor grade chlorosilane precursors have properties that are very suitable for use in SiC epitaxy at high temperatures (1100 C<T<2500 C). A particularly desirable feature is that compared to SiH₄, chlorosilanes have a reduced tendency towards homogeneous reactions in the gas phase which can result in defects in the deposited epitaxial material [1].

Demonstrations of three variants of chlorine-based CVD processes for α -SiC homoepitaxy have been reported in the technical literature. There is the chlorosilane approach, such as Si₂Cl₆ and propane [2], the hydrogen chloride approach using SiH₄, propane and HCl [3], and the halocarbon approach, for example SiH₄ and MeCl [4]. At Dow Corning, chlorosilane-based chemistries have been successfully implemented to deposit high quality (thickness

variations <2%, doping variations 7-15%, background doping <10¹⁴/cm³, contact layer doping >10²⁰/cm³) SiC epilayers in both R&D and production epitaxy equipment [5].

EXPERIMENTS

Modeling of HCl/chlorosilane/hydrocarbon/halocarbon epitaxy equilibrium reaction compositions was performed using Outokumpu HSC Chemistry for Windows (Outokumpu Research Oy, Finland). While most the CVD processes for SiC epitaxy operate under surface kinetics control, it is believed that the equilibrium reactions and compositions are insightful for understanding SiC epitaxy in hot wall CVD systems.

SiC homoepitaxy was performed on eight degree tilted 4H n+ SiC substrates in either single wafer or multiwafer hot wall epitaxy equipment. Epitaxial films with thickness ranging 3-50 um were deposited at rates of approximately 4-8 um/hr. Films were characterized using infrared spectroscopy, capacitance-voltage measurements, DLTS, and microwave photoconductive decay.

DISCUSSION

CVD Decomposition Chemistry for SiC Homoepitaxy

The thermal decomposition of simple silicon chloro-hydrides, propane and hydrogen at temperatures greater than 1400 C will result in the formation of SiC epilayers and effluent gases which would primarily include unreacted silicon gases, methane, hydrogen chloride and hydrogen. Generically this reaction can be written

$$xH2 + H_{(4-x)}SiCl_x + C_3H_8 \rightarrow SiC + 2CH_4 + xHCl + 2H_2 \quad (0 \le x \le 4)$$

$$\tag{1}$$

This reaction indicates at in addition to SiC, the primary reaction products are methane and HCl, and that the number of moles of HCl generated is tied to the number of chlorine atoms attached to the silicon source molecule. What is not apparent from Eq. (1) is the formation of intermediate species that will influence the growth of epitaxial layers.

The principle dissociation mechanism of these simple silicon molecules will result in the generation of silylene species of generic form $SiH_{(2-x)}Cl_x$ [6,7]. These species are the primary silicon building block for film growth, inserting at a –H or –Cl site on the surface of the substrate and generating H₂ or HCl by-products.

Although similar in structure and atomic composition, different silicon precursors will decompose via different primary dissociation reactions [6]. For H-Si-Cl type precursors the primary reaction path is silylene generation, although some free radical dissociation is possible. For SiCl₄ precursor, free radical dissociation is the most likely reaction. The temperature dependence of the reactant compositions were investigated by modeling the equilibrium reaction. The formation of Si vapor was included in all models. For hydrocarbons such as propane the assumed dissociation path generates CH_4 and $\cdot C_2H_5$, and for MeCl, CH_4 and Cl. In this work the formation of Me-Si species was assumed not to occur at a significant level (very low concentration) so as to control the formation of the epitaxial layer [6]. Table I shows the primary silicon reactions used in the equilibrium models. In the presence of chlorine, the gaseous Si-H intermediate species convert to Si-Cl species as this is a more stable molecular arrangement. In all cases listed in Table I, the inevitable species contributing to the SiC growth will be a silylene of generic form $SiH_{(2-x)}Cl_x$.

The SiC epitaxial growth conditions were studied using parameters commonly reported in the literature and these are summarized in Table II. These conditions represent inlet C/Si ratio of one. When HCl was included, it was done so that the ratio Cl/Si=4 to allow comparison to SiCl₄ processes. The model of the MeCl halocarbon chemistry, the C/Si=1 ratio was maintained.

Table I. Silicon based dissociation reaction paths for three growth variants used in α -SiC homoepitaxy.

Si-H-based							
Path/Order	Silylene	Free Radial					
Primary	$SiH_4 \rightarrow SiH_2 + H_2$	SiH₄→SiH₃ + H					
	Si-H-based With HC	l Present					
Secondary	$SiH_2 + 2HCl \rightarrow Cl_2SiH_2$	$SiH_3 + HCl \rightarrow ClSiH_3$					
Tertiary	$Cl_2SiH_2 \rightarrow H_2 + SiCl_2$	$ClSiH_3 \rightarrow H_2 + HSiCl$					
Si-Cl-based							
Path/Order	Silylene	Free Radical					
Primary	$ClSiH_3 \rightarrow H_2 + SiHCl$	$SiCl_4 \rightarrow SiCl_3 + Cl$					
	$Cl_2SiH_2 \rightarrow H_2 + SiCl_2$						
	$Cl_3SiH \rightarrow HCl + SiCl_2$						
Secondary		$SiCl_3 + HCl \rightarrow HSiCl_3$					
Tertiary		$HSiCl_3 \rightarrow HCl + SiCl_2$					

Table II. Reactant and process conditions used in modeling SiC epitaxy chemistry.

Material	Value
H ₂	2 mols
Si Precursors	0.0015 mols
C Precursors	0.0005-0.0015 mols
HCI	0.006 mols
Pressure	0.2 bar
Temp	500-1800 C

Table III. Key Si and C species contributing to SiC growth chemistry at equilibrium conditions.

Input	H2 + SiH4 +		H2 + SiH4 +		H2 + SiCl4 +		H2 + SiH4 + MeCl \rightarrow		
Chemistry	0.333*C3	0.333*C3H8 → SiC		0.333*C3H8 + 4HCl		0.333*C3H8 → SiC		SiC	
			\rightarrow	SiC					
Туре	Si	С	Si	С	Si	С	Si	С	
Species	SiH ₂	CH ₄	SiH ₃ Cl	CH_4	SiCl ₂	CH_4	SiH ₃ Cl	CH_4	
_	SiH_4		SiCl ₂		Si(g)		SiCl ₂		
	Si		SiHCl		-		SiHCl		
			Si(g)				Si(g)		

				SiH ₂				SiH ₂	
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Table III lists the model results of the species present to a concentration of 0.1% relative for each reaction. These species are the primary components assigned to the growth reaction.

The relative concentration of methane and Si vapor generated in each reaction was very comparable. Addition of a separate Cl precursor to SiH_4 -based processes appears to generate the same key species whether it is HCl or MeCl. Among the Cl-containing processes, the halocarbon chemistry generates relatively higher SiH_2 and relatively lower amounts SiHCl species.

Using the information obtained from equilibrium modeling, the C/Si ratio at the wafer surface was estimated for each reaction [8].



C/Si Ratio At Surface Precursor Impact

Figure 1. Calculation of the gas phase C/Si ratio at the wafer surface using equilibrium reaction data for the reactions in Table III.

Recalling that the inlet C/Si ratio was set to one in all models, it appears that while the different chemistries for epitaxy share common species, the reaction pathways lead to different growth conditions, especially at temperatures below 1600 C. The temperature dependence of the C/Si ratio values reflects the higher energy required to dissociate SiCl₄ compared to SiH₄, the chlorination of SiH₄ decomposition products, and the reaction path assumed for the MeCl-based process. Referring to the figure, inflections near 1225-1425 C can be linked to process chemistry driven, temperature dependent minimum in methane fraction and process chemistry driven, temperature dependent maximum in Si-Cl species fractions. At temperatures above 1800 C, the C/Si ratios of the different chemistries begin to converge. The result for the SiH₄-propane-HCl and SiH₄-MeCl process shows that the chemistry tends to lower value C/Si ratio at the surface for temperatures above 1400 C. This observation may shed light on the published observations that the SiC epitaxial film morphology improves compared to SiH₄-propane processes without chlorine additives [3,4].

The effect of the presence of Cl-containing species on the growth rate in SiC



homoepitaxy warrants discussion. Figure 2 is a survey of published growth rate data and Dow



Growth Rate per Mol Fraction Si vs Process

Corning data, where the combined set includes silane, silane and HCl and chlorosilane processes at different silicon precursor flow rates.

Figure 2. Survey of published growth rate results on Cl and non-Cl based SiC homoepitaxy with Si mol fraction range 0.02-0.10. In the left figure, box height is determined by the silicon precursor flow range, on the right the silicon precursor flow is normalized. SW=single wafer ; Batch=multiwafer (3-5 wafers).

In most published work on SiC epitaxy, the growth rate is a linear function of the precursor partial pressure, or said another way the growth rate/partial pressure is a constant. The right side of Figure 2 plots this metric for the growth rate data, a sort of efficiency metric.

Inspection of Figure 2 shows that for concentrations reported in the literature, the addition of HCl to SiH4-propane chemistry does not make significant change to the growth rate compared to the increased silicon precursor flow. Inspection of the data used to compile Figure 2 shows that 1) the partial pressure of SiH_4 used is >100x higher than the critical concentration at which gas phase nucleation is known to occur [9] and 2) the partial pressures of HCl were below that of SiH₄. Bloem reported that HCl can be added to SiH₄-based silicon epitaxy processes in order to suppress gas phase nucleation and increase the growth rate [10]. In Bloem's work, the magnification of growth rate with partial pressure ratio for $0 < (P_{HCl}/P_{silane}) < 1$ should be approximately 1.5-3x. It was also shown that the amount of HCl used has to be increased at higher temperatures to keep the same impact on gas phase nucleation and growth rate. In Figure 2, the SiC epitaxy data corresponds to conditions of 0.3<(P_{HCl}/P_{silane})<1 and 1550<T(C)<1600. In these examples, the amount of growth rate change expected from the addition of HCl to SiH₄/propane should be small and that is what is observed. The graph on the right side of Figure 2 supports this fact, the HCl-based chemistry shows incremental efficiency improvement. Since the growth temperatures for SiC epitaxy are higher than silicon epitaxy, if it is intended that the HCl suppress the loss of growth rate from particle formation, higher concentrations of HCl are likely required. More interesting in the right figure is the generally higher efficiencies of the chlorosilane processes. It is proposed that the higher efficiency in the chlorosilane growth is a result of the direct dissociation path which produces highest mol percentage of SiCl₂ species, whereas in the SiH₄-HCl type processes this is a tertiary reaction. The high efficiency plotted for the SiH₄-MeCl process may be a slight overestimate since not all of the growth data was available in the reference and the equilibrium models predict lower SiCl₂ mol percent than chlorosilanes.

The gas phase nucleation of SiH₄ and the use of graphite parts is a major concern for particle-related defect formation in SiC epitaxy. Several publications have studied the propensity of SiH₄ to undergo gas phase nucleation at T>1000 C for conditions typical to silicon epitaxy. The critical SiH₄ concentration for gas phase nucleation decreases with increasing temperature [9] and is estimated at 0.001-0.002 volume percent above 1550 C, a level lower than that typical of SiC epitaxy process reactant compositions (10-40 sccm SiH₄, 3-10 sccm C₃H₈, 30-80 slm H₂). The formation of silicon particles can degrade the growth rate and defect density in SiC epitaxy processes [11]. Little is published correlating Si precursor chemistry and particle generation in SiC epitaxy, while it is common practice to use precursor choice as a means of defect control in silicon epitaxy.

Modeling of gas phase nucleation in SiC epitaxy shows that the particle volume clusters in the reaction areas where the temperatures are typically T<1300 C [11]. This condition occurs slightly above the wafer in a cold wall vertical CVD system or upstream in a horizontal hot wall CVD system, at the low temperature end of the direction of maximum temperature gradient. The formation of the particles is associated with supersaturation and polymerization of SiH species. From the silicon precursor perspective, minimization of the Si vapor and SiH_x silylenes will limit the chances for particle formation in the SiC epitaxy process. At the same time, accentuation of the SiCl_x species with lower vapor pressure will help to minimize the opportunity for supersaturation. Figure 3 plots the equilibrium model data for the mol percent sum for Si vapor and SiH₂ corresponding to the reactions in Table II. The figure shows addition of HCl or MeCl to SiH₄-propane chemistry at Cl/Si ratio range 1-4 is not as effective to reduce species which promote gas phase nucleation as the use of SiCl₄.



Figure 3. Equilibrium results of the sum of mol percents of Si vapor and SiH_x vapor as a function of temperature.

Experimental Results for Chlorosilane CVD-based SiC Growth and SiC Films

Results for chlorosilane based SiC homoepitaxy chemistry performed on both single wafer and multiwafer hot-wall CVD systems were initially reported in 2005 [5]. Figure 4 compares the SiC epitaxial growth rates in a horizontal single wafer CVD system measured on 76mm wafers for several chemistries. Over a growth rate range of 1-20 um/hr, it was found that the chlorosilane growth rate is linear with chlorosilane partial pressure and slightly higher the silane growth rate at equivalent partial pressure.

Investigations of doping control were performed to compare the effect of silicon precursor on the background dopant incorporation and p-type dopant control. This data is presented in Figure 5. The data indicates that the basic trends of dopant incorporation are similar



Figure 4. SiC growth rate vs. silicon precursor partial pressure for several SiC homoepitaxy chemistries. Propane was the carbon source used in all cases.



Figure 5. Impact of silicon precursor on dopant incorporation for homoepitaxial SiC films. The left figure shows effects on background doping in both horizontal single wafer (SW) and multi-wafer (MW) CVD systems, propane is the carbon source. The right figure compares p-type doping using TMA for chlorosilane/propane epitaxy in a multi-wafer CVD system to SiH4/propane epitaxy [12].

for the chlorosilane-based and silane-based chemistries.

Testing of the electrical defects and carrier lifetimes in the SiC epilayers grown by chlorosilane chemistry has shown some interesting initial results. Table IV lists some emerging data comparisons between SiH₄ and chlorosilane chemistries.

Table IV. Trends for electrical defects in SiC epitaxially grown films from various precursor chemistries.

Metric	SiH4-Chemistry Values	SiCl-Chemistry Values	[REF]
Concentration of Deep	Z1/Z2: $5x10^{12}$ /cm ³	Z1/Z2: $1x10^{12}/cm^3$	[13,16]
Centers by DLTS	EH6/7: $3x10^{12}$ /cm ³	EH6/7: $2-5 \times 10^{11}$ /cm ³	
Minority Carrier			
Lifetime by μ -PCD and	<0.15 μs	0.25-0.50 μs	[14]
EBIC ($10 < t_f (um) < 40$			
Dependence of Deep	Z1/Z2 Concentration	Z1/Z2 Concentration	[15]
Center Concentration on	decreases as C/Si Ratio	decreases as C/Si Ratio	
Gas Phase C/Si Ratio	increases	increases, but lifetime not	
		dependent on Z1/Z2	
		D-center increases as C/Si	
		ratio increases.	
Defects Limiting	Z1/Z2, D-Center (Boron)	Lifetime insensitive to Z1/Z2	[15,18]
Minority Carrier		Concentration, but inversely	
Lifetime		proportional to concentration	
		of D-Centers.	

These initial results show that the mechanisms for formation of deep level electrical defects may be different between SiH_4 and chlorosilane chemistries. At this stage there is no available explanation for this behavior, but the findings warrant additional exploration.

CONCLUSIONS

Chlorine-based chemistry is a promising method for use in the CVD growth of high quality SiC homoepitaxial films. It is anticipated that the use of chlorine containing molecules can help to control gas phase nucleation similarly to the same strategy applied for silicon epitaxy in the 1970's. Modeling and experimental data for SiC epitaxy processes show that the usage of chlorosilane molecules can yield high growth rates and possibly more margin for particle control compared to the addition of non-silicon based chlorine source in a legacy SiC epitaxy chemistry. Halocarbon processes give similar growth results to chlorosilanes, but may have limited flexibility to control the Cl/Si ratio independent of the C/Si ratio. Finally, initial testing of the formation of deep level defects in chlorosilane based SiC films shows that the formation mechanisms may differ from legacy SiH4/propane type processes.

ACKNOWLEDGEMENTS

The measurement support and discussions of the EMEG team at Carnegie-Mellon University are gratefully appreciated.

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