Horizontal hot wall reactor design for epi-SiC growth

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The model adopted for the simulation of a new industrial size type of horizontal cold wall reactor for epitaxial silicon carbide deposition is reviewed. The attention is focalized on the chemical mechanism adopted and on the comparison with some growth rate data and temperature profiles for the system ethylene, silane, hydrogen and the deposition of undoped silicon carbide.

1 Introduction

Silicon Carbide (SiC) is the material of the new generation for the high power, high frequency and high temperature applications. In the last decade many efforts were done to improve and upgrade the material quality, both for the bulk and epitaxial growths. Up today, the determining step for the Silicon Carbide industrial application is the poor wafer quality obtained from the boules grown by the sublimation techniques. Accordingly, the deposition of a high quality epilayer is still needed to satisfy the microelectronic market requests. In this optic, the Chemical Vapor Deposition is the only industrial available technique for the deposition of a very high quality layer also for SiC.

In this paper the simulation of the Silicon Carbide epitaxial deposition performed in a hot wall reactor type is presented. Industrially, deposition profile and film quality are the only performance parameters of interest. Both of them are determined by pressure, temperature and precursors concentration profiles inside the reactor. Thus, to obtain an accurate process description both the temperature field and the chemistry involved have to be correctly simulated.

The attention was here focused on a new type of horizontal reactor with rotating susceptor. This reactor can hold up to 6x2" or 4x3" wafers due to the dimensions of its susceptor (i.e., about 20 cm). Standard process conditions for the system hydrocarbon, silane and hydrogen as carrier gas are pressure within the interval 0.1-0.2 atm and temperature within the 1500°C-1800°C. The examined process conditions are the pure CVD ones, that is the inlet mole fractions were selected to avoid the well known homogeneous nucleation phenomenon [1-3].

Previous simulations demonstrated that the fluid dynamic conditions are in the fully developed laminar regime (i.e., Re about 30) and no recirculation and flow non idealities are present in the deposition zone [2,3]. Thus for the, simulation of the process conditions, to speed up the whole process and to be compatible with the industrial needs, a simplified 1D model was adopted. More emphasis was placed in the development of the chemical mechanism involved in the deposition. While some previous work well addressed the gas phase chemistry [4,5] some questions were still present about the surface chemistry and in particular about the formation of not stoichiometric films. In particular a new series of surface reactions was introduced responsible for the Si, Si_2C, SiC_2 sublimation and the formation of non stoichiometric crystal portion. That was possible allowing the formation of two fictitious solid species, identified as $SiC_{2(s)}$ and $Si_2C_{(s)}$, with the aim to mimic the formation of carbon and silicon rich island on the growing film. Finally, the model predictions were compared with growth rate data obtained in the above described reactor.

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2 Reactor modeling

As pointed out in the introduction, all the simulations were here performed through a simple 1D model that has the advantage to allow a fast investigation of all the kinetic aspects also when adopting complex kinetic schemes. In agreement with the results of previous simulations [2,3] the investigated domain of the reduced model was selected as sketched in figure 1a, considering only the reactor portion at constant section where the gas heating started. The model involves the mass conservation equations for any species involved in the deposition mechanism to describe the gas phase and the surface composition profiles and the energy conservation equation to describe the evolution of the gas temperature within the system and its detailed description can be found in [6,7]. However, due to the nature of the reactor here considered, the deposition was allowed on all the hot walls and not only on the susceptor. Besides the derivation of the deposition mechanism to be embedded in the model whose description will be reported below, the transport parameter involved were all estimated through the Lennard-Jones parameters for all the species involved in.

Lastly, the effect of susceptor rotation was accounted for in the estimation of the involved mass transport coefficients (with an almost negligible consequence) and finally in the azimuthal averaging of the growth rate profile.
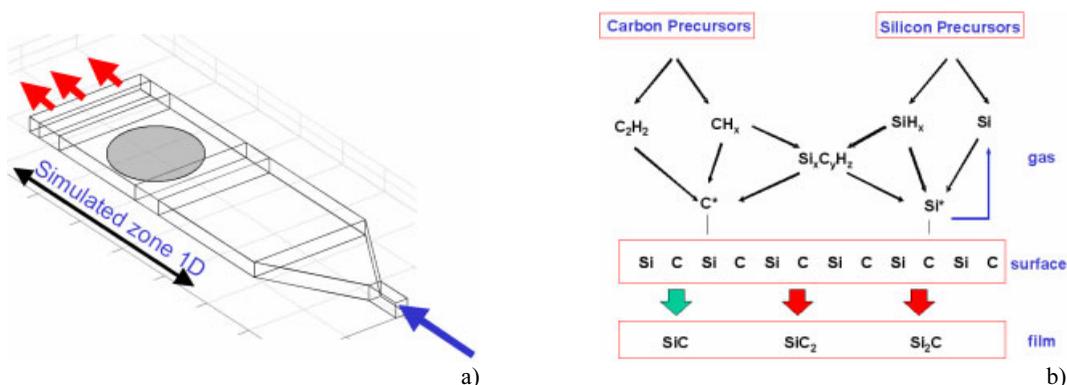

Fig. 1 a) sketch of the simulated zone by the 1D model. b) Main reaction pathways involved in the epitaxial SiC deposition mechanism (silicon species adsorbed on surface carbon and vice versa).

3 Deposition mechanism

Usually the Silicon Carbide epitaxial layers are grown from propane or ethylene and silane. The deposition mechanism can be divided in three sections: one related to the hydrocarbon cracking, one to the silane decomposition and the latter to the reaction between the products previously obtained to form the organosilicon compounds. The hydrocarbon cracking mechanism is well known from combustion chemistry while silane decomposition was extensively studied for the silicon processes. Reaction between hydrocarbon and silicon compounds were not very well investigated and yet few data are available in literature. Among the gas phase mechanisms found in literature linking the above mentioned parts, the one developed for epitaxial deposition at high temperatures was here selected because more in agreement with the aims and the growth conditions here examined [5].

A common problem related to the SiC process deposition from silane is the homogeneous gas phase nucleation that originates the undesired formation of particulate (e.g., liquid silicon droplets or SiC particles). This phenomenon causes a depletion of the reactants available for the growth, and more important could influence the surface quality of the material deposited because the particulate impinging on the surface. However, in the case here considered, due to the high carrier gas flow rate and the very low concentration of the precursors, the nucleation of condensed phases in the gas could be considered negligible.

More attention was placed on the development of the surface deposition mechanism, and in particular to the possibility of formation of not stoichiometric films, like for III-Vs. Here, the physical and chemical processes occurring on the surface are: adsorption, desorption, dissociation, diffusion, island formation and growth. At present a detailed description of all those phenomena is not present in literature, not even for the more simple ones like adsorption and desorption. Accordingly, as pointed out in the introduction, a new surface chemical mechanism was here developed considering the adsorption of all the gaseous species, the contemporary sublimation of gaseous Si, Si_2C and SiC_2 from the growing surface and the formation of non stoichiometric portions of the crystal lattice. This point was accounted for by introducing in the lattice, in addiction to $SiC_{(s)}$,

two "formal" species (e.g., $Si_2C_{(s)}$ and $SiC_{2(s)}$) with the aim to mimic the formation of silicon-rich and carbon-rich portions of the lattice. A simplified sketch of the main features of the adopted deposition chemistry is illustrated in Figure 1b. Because the large number of reactions involved in the original mechanism, it is unlikely that all them play a significant role. Accordingly, the main reactions pathways were identified and a lumped mechanism was developed through a sensitivity analysis procedure [3]. Thus, the lumping procedure reduces the gas phase species from 36 to 10 while keeping 8 surface species. In terms of reactions, gas phase ones moves from 138 to 18, and surface ones from 28 to 31, as summarized in Table 1.

Table 1 Lumped deposition mechanism for epiSiC growth ($1 and $2 Si, C surface sites,* adsorbed species). $k = AT^b e^{-E/RT}$, with parameters coherent with rates in mol/cm^2/s, gas and surface concentrations in mol/cm^3 and mol/cm^2, activation energy in cal/mol. All forward reactions.

Hydrocarbons gas	$Log_{10}A$	b	E_a	surface	$Log_{10}A$	b	E_a
$C_3H_8 = C_2H_5 + CH_3$	22.32	-1.80	88693	$CH_4 + \$1 = C^* + 2 H_2$	7.62	0.5	0
$C_2H_5 + CH_3 = C_3H_8$	13.65	0.00	0	$CH_3 + \$1 = CH^* + H_2$	11.93	0.5	0
$C_2H_5 = C_2H_4 + H$	12.40	0.40	37200	$C_2H_5 + 2\$1 = C^* + CH^* + 2H_2$	20.76	0.5	0
$C_2H_4 + H = C_2H_5$	11.66	1.50	990	$C_2H_4 + 2\$1 = 2C^* + 2H_2$	17.97	0.5	0
$C_2H_4 = C_2H_2 + H_2$	27.90	-3.50	88759	$C_2H_2 + 2\$1 = C^* + H_2$	19.08	0.5	0
$C_2H_2 + H_2 = C_2H_4$	2.49	2.78	38945	$SiH_2 + \$2 = SiH_2^*$	11.78	0.5	0
$CH_4 = H + CH_3$	13.92	0.00	103812	$SiH_4 + \$2 = SiH_2^* + H_2$	10.50	0.5	18678
$CH_3 + H = CH_4$	14.98	-0.40	0	$SiH + \$2 = SiH^*$	11.79	0.5	0
$CH_3 + H_2 = CH_4 + H$	2.36	3.12	8711	$Si + \$2 = Si^*$	11.80	0.5	0
$CH_4 + H = CH_3 + H_2$	4.12	3.00	8037.4	$2 CH^* = C^* + H_2$	24.36	0	61000
$2 CH_3 = C_2H_5 + H$	20.56	-1.98	26377	$2 SiH^* = Si^* + H_2$	24.36	0	61000
$C_2H_5 + H = 2 CH_3$	2.76	3.57	0	$SiH_2^* = Si^* + H_2$	24.36	0	61000
$CH_4 + CH_3 = C_2H_5 + H_2$	13.01	0.00	22850	$H + Si^* = SiH^*$	12.30	0.5	0
$2H + M = H_2 + M$	18.73	-1.30	0	$H + C^* = CH^*$	12.55	0.5	0
Silane gas	$Log_{10}A$	b	Ea	$Si^* + C^* = SiC + \$1 + \$2$	17.00	0	0
$SiH_4 + Si = 2SiH_2$	13.97	0.00	1987	$Si^* = \$2 + Si$	13.00	0	40500
$SiH_4 = SiH_2 + H_2$	29.82	-4.79	63450	$H_2 + 2\$2 = 2H^*$	11.36	0.5	0
$SiH_2 = Si + H_2$	11.42	-0.88	45000	$2 CH^* = C^* + H_2$	23	0	61000
$SiH_2 + H = SiH + H_2$	13.14	0.00	2000	$H + CH^* = C^* + H_2$	12.55	0.5	0
				$CH^* = 0.5 H_2 + C^*$	23	0	57100
				$2CH^* = C_2H_2 + 2 \$1$	23	0	87954
				$CH^* + H_2 = \$1 + CH_3$	11.36	0.5	87954
				$CH^* + H^* = H_2 + \$2 + C^*$	23	0	61000
				$CH^* + 0.5H_2 = C^* + H_2$	12.36	0.5	0
				$2C^* + H_2 = 2CH^*$	12.36	0.5	0
				$2 SiH^* = Si^* + H_2$	25	0	61000
				$SiH_2^* = Si^* + H_2$	25	0	61000
				$H^* + H^* = H_2 + 2 \$2$	23	0	61000
				$2Si^* + C^* = Si_2C + 2\$2 + \$1$	24.00	0	0
				$Si^* + 2C^* = SiC_2 + \$2 + 2\$1$	24.00	0	0
				$SiC_2 + 2\$1 + \$2 = 2C^* + Si^*$	11.67	0.5	0

4   Discussion and conclusion

The examined experimental system uses C_2H_4 and SiH_4 as carbon and silicon precursors, respectively, and H_2 as reactive carrier gas. The conditions simulated here refer always to an inlet with C/Si = 1.5 and Si/H_2 = 0.0002. The system pressure was set to 0.1 atm, while the maximum wall temperature value was set to 1550°C or 1600°C and the carrier flow rate was varied from 100 slm to 150 slm, depending by the considered run. The growth rate profile along a hot wall reactor is usually determined by the precursors mass flux towards the deposition surface but it is affected also by the "etching and sublimation" features induced by the hot walls antecedent the area holding the substrates. Thus, for a comparison, it is important the availability of a reliable wall temperature profile as the one illustrated in Figure 2, where the wall and the gas temperatures, as well as the growth rates are scaled with respect their maximum values. As illustrated by the data reported in figure 2, the calculations satisfactory match the experiments, demonstrating the reliability of the transport and of the chemical parameters embedded in the reactor model. In fact, it is important to consider that no fitting of the involved parameters was performed on these particular data sets.

As general conclusions, the simulations confirmed that the calculated profiles are almost insensitive to the carbon precursor adopted (e.g., propane or ethylene) because the gas phase species distribution reaches that of thermodynamics equilibrium. Accordingly, the only parameters to keep under control are the molar ratios between carbon, silicon and hydrogen.

About the reactor features, it can be concluded that in the examined one, the susceptor is placed always in the deposition region because positive growth rates are observed and their decreasing trends can be explained in terms of precursors depletion. Moreover, the growth rate profile exhibits a maximum only for the higher flow rates because the shift in the gas heating due to the reduced residence time.

In conclusion the adopted reactor model and the involved parameters can be considered reliable to design the second release of the examined reactor.
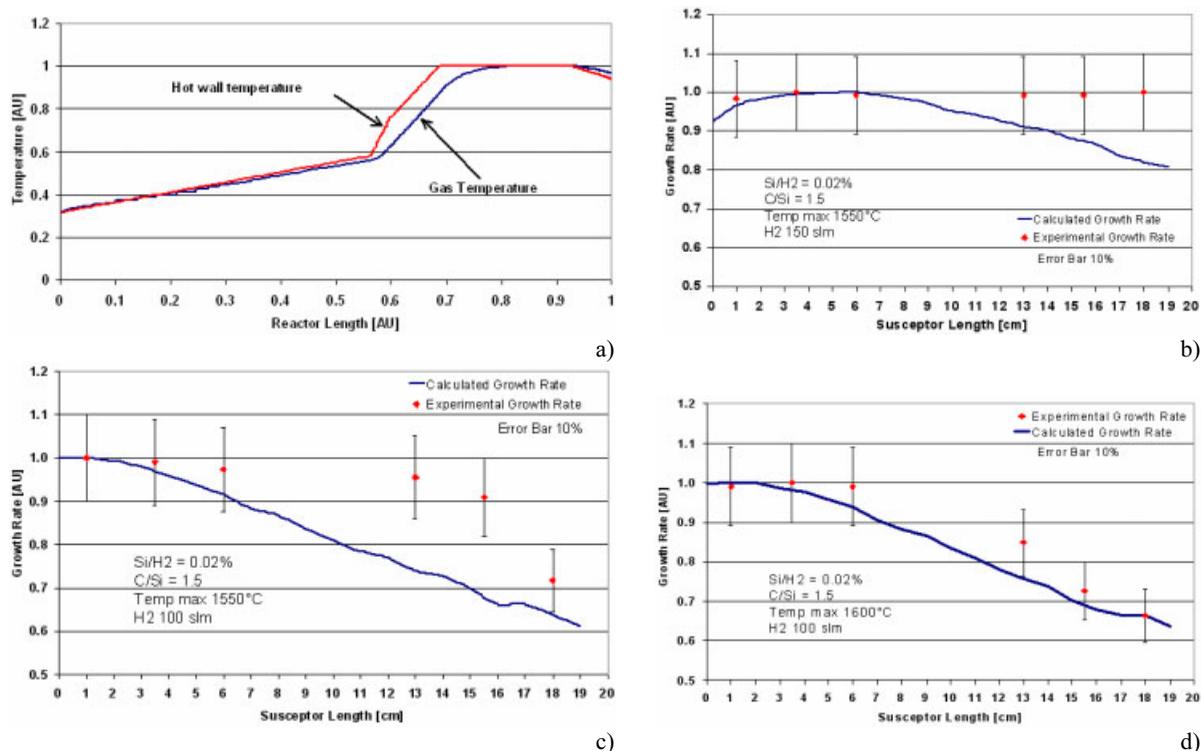

Fig. 2 Comparison between calculated and experimental growth rate profiles along main reactor coordinate for different operating conditions. Inlet C/Si = 1.5, Si/H_2 = 0.0002, Pressure = 0.2 atm. (a) wall temperature profile along susceptor; (b) H_2 flow rate 150 slm, wall max temperature 1550°C; (c) H_2 flow rate 100 slm, wall max temperature 1550°C; (d) H_2 flow rate 100 slm, wall max temperature 1600°C.

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