Multiscale investigation of the influence of surface morphology on thin film CVD

A. Barbato, A. Fiorucci, M. Rondanini, and C. Cavallotti

Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta",
Politecnico di Milano, via Mancinelli 7
20131 Milano, Italy

ABSTRACT

We show that the morphological evolution of an epitaxial Si film deposited in a CVD reactor can have a significant impact on the growth rate affecting the surface reactivity. We base such conclusion on simulations performed using a multiscale CVD model in which we coupled consistently the gas phase and surface dynamics. In particular at the macroscale we solve overall mass, momentum, and energy balances with the finite element method, while at the microscale the morphological evolution of the film is investigated with 3D kinetic Monte Carlo. Macro and micro scales are linked together imposing continuity of gas phase concentrations and fluxes at the common boundary. The surface model implemented in KMC takes into account the Si(100)2x1 surface reconstruction, and the anisotropic diffusion of H and Si adatoms and dimers.

Keywords: LPCVD, Multiscale, KMC, Silicon, FEM

1 INTRODUCTION

The continuous enhancement of the technology of deposition of semiconductor thin films is among the fundamental paradigms of the microelectronic industry. The progressive reduction of the size of interconnection trenches is a measure of the constant progress of technology in this sector. As the characteristic size of microelectronic devices approaches systematically the nanometres scale the need for the understanding of the atomistic processes responsible for the film growth increases correspondently.

Most of the models of Chemical Vapor Deposition (CVD) reactors, proposed in the literature and used to predict the film growth are based on the solution of macroscopic momentum, energy and mass conservation equations by means of finite element method (FEM). The gas phase and surface chemistry is usually described in these models by means of kinetic schemes consisting of elementary or effective reactions, depending on the knowledge of the considered system [1,2]. While such models can describe accurately the gas phase, they give only an approximate description of the reactive surface. In fact modeling the surface chemistry at the same scale length used to model gas phase implies the loss of any morphological information of the evolving surface. For this reason a more effective approach is represented by multiscale modeling. Multiscale models take advantage of different modeling approaches and tools, to describe chemical physical phenomena that occur at different scales. Several multiscale models have been proposed recently in the literature to improve the description of surface processes in CVD of thin solid films, among which we remember here the works of Derby [3], Jensen[4] and Vlachos[5,6].

In this work we propose a new multiscale model in which we couple consistently the reactor scale description of transport and gas phase chemistry with an atomistic description of the surface chemistry based on the kinetic Monte Carlo (KMC) approach. The developed approach was applied to the study of the surface morphological evolution of Si on the Si(100) 2x1 surface, a system for which kinetic and transport properties of adsorbed species are rather well know.

2 METHOD AND THEORY

The multiscale model here implemented is composed of two different parts, one meant to describe phenomena relevant at the macroscale, while the other is based on the description of the surface morphological evolution.

At the macroscale finite elements method (FEM) are used to solve energy, momentum and mass conservation equations for gas phase chemical species. The inputs to the model are the geometry of the LPCVD reaction chamber, the thermodynamic and transport properties of each considered chemical species, the gas phase kinetic scheme and its parameters, and the boundary conditions for each domain modeled. The resulting set of non linear equation is solved in an axial symmetry domain within a mesh composed of biquadratic elements. Since the system is dilute, the solution of energy and momentum are decoupled from the mass conservation equation [4,7]. This allows calculating in a first run the flow and heating profile, and then solving the conservation equation of total mass and individual species to obtain the concentration profile and the mass fluxes of each gas phase species over the growth surface, which are used as input for the microscopic simulations.

A 3 dimensional, grand-canonical, kinetic Monte Carlo method was implemented in order to reproduce the

microscopic surface evolution during the growth process. In particular, our KMC implementation follows the theory outlined by Fichthorn and Weinberg[8], which involves direct tracking of real-time and a rejection-free choice of the random transition. In this way we can reproduce the evolution mean properties, both temporal and morphological, of a growing surface and the behavior of adsorbed hydrogen, as shown previously by Cavallotti [9]. The KMC model takes as input the mole fractions of the reactive gas species over the surface, from which it calculates the mole fluxes, in terms of mono layers per second, for each atomic species that can adsorb on the surface. The system reproduced is a finite lattice with the shape of a rectangular parallelepiped with periodic boundary condition on the x and y axes, and the z dimension variable during simulation, because of the continuous adsorption of gas phase Si atoms.

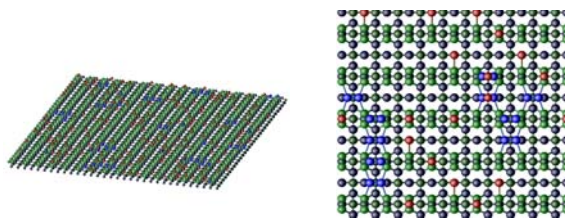

Figure 1. An example of the surface simulated with KMC. Dark, green, blue and red spheres represent bulk Si atoms, surface Si atoms, adsorbed Si atoms and adsorbed Hydrogen respectively.

The Kinetic Monte Carlo code is able to simulate three different events: adsorption, diffusion and desorption. In Tables 1-3 are reported all the kinetic parameters used in the KMC simulation. The probability of every event to occur is related to its rate. In fact, the choice of a random move is made by searching, in a binary tree a rate that has a value lower than the one generated by multiplying for a pseudo-random number the sum of all possible transition rates. Adsorption rates are calculated applying the kinetic gas theory on the basis of the mole fraction obtained from the macroscale simulations. The mass fluxes calculated in this way are then multiplied by a temperature dependent sticking coefficient. A peculiarity of the Si(100) 2x1 surface is the presence of adsorbed dimers, which formation and diffusion was considered explicitly in the KMC model. On the surface, adsorbed dimers are formed when two atoms of silicon are in vicinal position and aligned perpendicularly to the underlying dimer rows. After that an ad-dimer is formed, it cannot divide or desorb from the surface, but it can diffuse to form the typical dimer rows that characterize the Si-100 surface [10]. Different diffusion rates are assigned to each adsorbed atom, (hydrogen, silicon and silicon dimers), depending on the directions of diffusion (parallel or perpendicular to substrate dimers rows) and kind, number and position of nearest-neighbors. The kinetic parameters for diffusion events are summarized in Table 2. Parameters related to diffusion of silicon dimers were taken from the literature and were mathematically and experimentally determined [11-13], while the ones related to single silicon were determined as reported in [10].

Table 1. Sticking coefficients expressed as $S=S_0\, e^{-Eatt/RT}$. The adsorption activation energy Eatt is reported in cal/mol.

Adsorption		
	S_0	Eatt
SiH_4	$1{,}18 \cdot 10^{-2}$	3000
SiH_2	1,0	-
H_2	$1{,}0 \cdot 10^{-8}$	-

Table 2. Diffusion kinetic constants expressed as k = Aexp-Eatt/RT . Eatt is the sum of E_{dir} and E_{NN} and is a function of direction (parallel or perpendicular to dimer rows) and number of neighbors. Pre-exponential factors and activation energies in s^{-1} and eV

Diffusion					
Species	A	E_{dir}		E_{NN}	
		//	⊥	1	2
Si	10^{13}	0,6	1,0	0,2	0,4
Dimer	10^{13}	1,0	1,4	1,6	1,8
H	10^{13}	1,8	1,8	0	0

Table 3. Kinetic constant of H_2 desorption expressed as $k=Ae^{-Eatt/RT}$, with Eatt in cal/mol and A in s^{-1}.

Desorption		
	A	Eatt
H_2	$2{,}5 \cdot 10^{15}$	57600

Simulations were usually started from a smooth surface in the absence of step edges and were continued till a steady state, characterized by the constant density of surface hydrogen atoms corresponding to the establishment of the Langmuir dynamic equilibrium was reached. Average growth rates were then calculated through the counting of the average free site fraction and of the silicon mole flux.

The coupling between macro and micro scale is an important step in order to obtain a consistent simulation model. In fact, we show in this paper that making simulation only at the macroscale it is impossible to reproduce accurately the chemical physical behavior of the studied system, and the same assertion can be made if just a microscale model is adopted. In our model, the coupling between the two scales is made by imposing the continuity of gas fluxes between the macro and micro-scale over n selected nodes of the FEM mesh in correspondence of the growth surface. For each of the n nodes a KMC simulation is performed, which takes as input the gas phase fluxes calculated with the macroscale model. In the simulations conducted to test the model we have performed KMC

simulation over 5 different equidistant points of the reactive surface. Mole fractions of gas phase species were taken as input for microscale simulation. After running the microscale simulations, mole fluxes of the species leaving the microscale are calculated and are used as boundary condition for the macroscale model. Macro and microscale simulations are iterated until convergence is achieved A stable convergent scheme is obtained by incorporating information about the jacobian contribution at the reactor-nodes boundary.

3 RESULTS AND DISCUSSION

The multiscale model was used to study the growth rate and surface hydrogen coverage experimentally measured by Greeenlief et al. [14,15] during the CVD of silicon from SiH_4. Film growth data were collected in a rapid thermal chemical vapor deposition (RTCVD) reactor, where the substrate temperature was imposed by a set of infrared lamps. Silicon films were grown at a flux of 0.01 slm of pure silane and pressures comprised between 0.3 and 3 mTorr; growth rates were measured at different susceptor temperatures. The CVD reactor used to perform the experimental measurement is described in details in [15]. The growth process consisted in a first phase in which the growth temperature and silane flow were established, after which the growth condition were maintained for 5 minutes. A rapid pump down of the reactor and cool down of the wafer was then used to freeze the surface hydrogen present at the end of the growth process, which was then measured.

The gas phase and surface chemistry was modelled through the set of four chemical reactions reported in Table 4. One reaction, the thermal decomposition of silane, occurs in the gas phase and three reactions, silicon growth and surface hydrogen desorption, at the surface-gas interface.

Table 4. Simplified kinetic mechanism inserted in the macroscale model. Units in term of mol, s, cal and rate constants expressed as $k=AT^{\alpha}e^{-Eatt/RT}$.

	A	α	Eatt
$SiH_4 \rightarrow SiH_2 + H_2$	$1{,}081 \cdot 10^{17}$	-0,87206	56685
$SiH_4 \rightarrow Si(s) + 4\underline{H}$	$1{,}18 \cdot 10^{-2}$	-	3000
$SiH_2 \rightarrow Si(s) + 2\underline{H}$	1.0	-	0
$2\underline{H} \rightarrow H_2$	$2.5 \cdot 10^{15}$	-	57600

The kinetic parameters for these reactions have been taken from the literature; the rate of decomposition of silane was taken from Dollet [16], the sticking coefficient of SiH_4 from Gates [17,18], for SiH_2 we assumed a unary sticking coefficient and no activation energy, kinetic parameters of hydrogen desorption were taken by Flowers [19]. In addition, to obtain a better reproduction of experimental data, we increased by a factor of five the sticking coefficient relative to SiH_4 suggested by Gates.

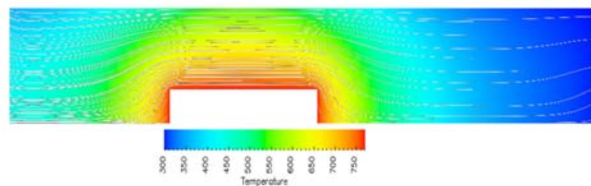

Figure 2. Geometry, temperature field and flow field of the simulated CVD reactor.

Due to the low pressure and modest temperatures, only a small amount of SiH_2 is produced in the gas phase, which indicates that gas phase reactions do not influence the growth rate. Also, at low temperatures the surface is fully covered by hydrogen; this causes low values of growth rate and the formation of an atomic rough surface. Raising the temperature the surface hydrogen coverage decreases and the growth rates increases.

By comparing the results produced by simulations performed only at the macroscale with experimental data reported by Greenlief [14,15], is possible to observe a qualitative agreement both for the growth rate and the hydrogen coverage. However the growth rate is underestimated at low temperatures and overestimated at high temperatures, and a similar trend can be observed for hydrogen coverage.

By comparing the data calculated using the multiscale model with the experimental data, it is possible to observe that the agreement is good at high temperatures, and gets worse as the temperature decrease. The disagreement is maximum in the temperature range in which there is transition between chemically controlled and silane diffusion controlled growth regimes (at about 850 K). At this temperature it is also possible to observe that also the surface hydrogen coverage in under evaluated.

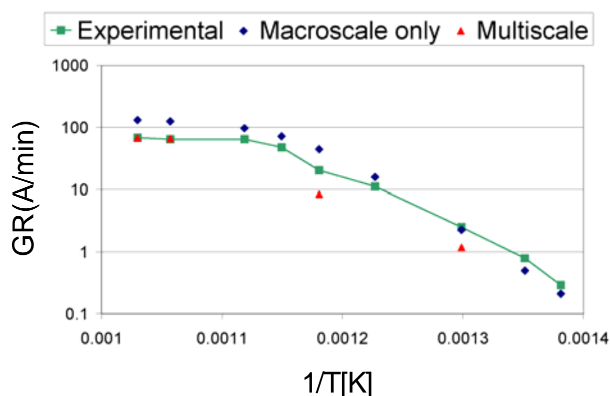

Figure 3. Growth rate versus 1/T. Units are K and A/min. In graph are reported experimental data (green line and square), values calculated by "FEM only" simulation (Blue rhombi) and values calculated by coupled simulation (Red triangles).

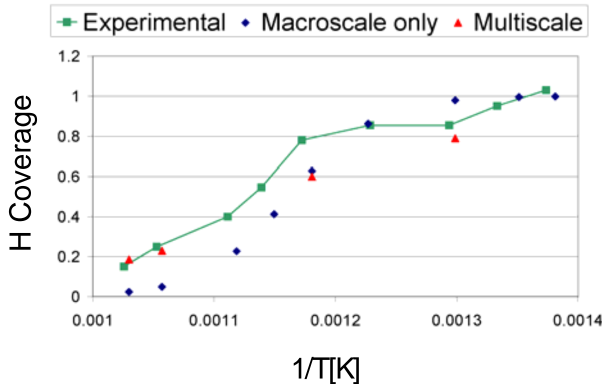

Figure 4. Hydrogen coverage versus temperature. Units are K and A/min. In graph are reported experimental data (green line and square), values calculated by "FEM only" simulation (Blue rhombi) and values calculated by coupled simulation (Red triangles).

This disagreement lead to considerate that there isn't a correct comprehension of the real mechanism by which hydrogen desorbs from surface.

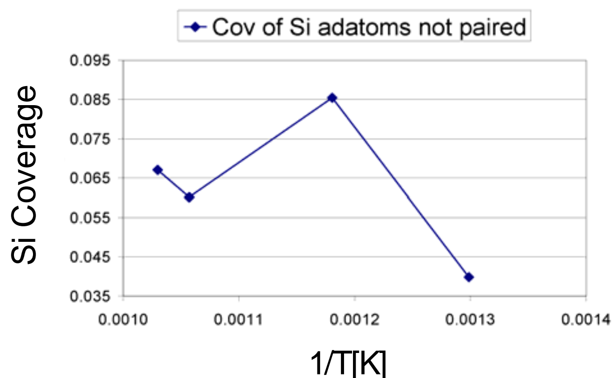

Figure 5. Mean coverage of adsorbed silicon adatoms not paired in dimers during simulation of deposition performed at four different temperatures. Unit is K.

4 CONCLUSIONS

A multiscale approach was used to study the silicon CVD on a Si(100) 2x1 surface. Calculation performed only on one scale brings disagreement between calculated and experimental data and gives no information about morphology of the grown film. Instead, data calculated with the coupled model can describe with great care the evolving surface morphology and, because of the correlation between morphology and growth rate, can reproduce better the experimental data.

However, a disagreement between two sets of data is reported. We suppose that this disagreement is due to the not complete comprehension of the real desorption mechanism of adsorbed hydrogen leaving the surface.

REFERENCES

[1] Hitchman, M.L. and Jensen, K.F. (1993) Academic Press, London.

[2] Carra, S. and Masi, M. (1998) Progress in Crystal Growth and Characterization of Materials 37, 1-46.

[3] Derby, J.J., Kwon, Y.I., Pandy, A., Sonda, P., Yeckel, A., Jung, T. and Muller, G. (2006) in: Interdisciplinary Transport Phenomena in the Space Sciences, Vol. 1077, pp. 124-145.

[4] Rodgers, S.T. and Jensen, K.F. (1998) Journal of Applied Physics 83, 524-530.

[5] Raimondeau, S. and Vlachos, D.G. (2002) Chemical Engineering Journal 90, 3-23.

[6] Lam, R. and Vlachos, D.G. (2001) Physical Review B 6403.

[7] Mihopoulos, T.G., Gupta, V. and Jensen, K.F. (1998) Journal of Crystal Growth 195, 733-739.

[8] Fichthorn, K.A. and Weinberg, W.H. (1991) Journal of Chemical Physics 95, 1090-1096.

[9] Cavallotti, C., Barbato, A. and Veneroni, A. (2004) Journal of Crystal Growth 266, 371-380.

[10] Mo, Y.W., Kleiner, J., Webb, M.B. and Lagally, M.G. (1992) Surface Science 268, 275-295.

[11] Brocks, G. and Kelly, P.J. (1996) Physical Review Letters 76, 2362-2365.

[12] Mattsson, T.R., Swartzentruber, B.S., Stumpf, R. and Feibelman, P.J. (2003) Surface Science 536, 121-129.

[13] Swartzentruber, B.S., Smith, A.P. and Jonsson, H. (1996) Physical Review Letters 77, 2518-2521.

[14] Greenlief, C.M. and Armstrong, M. (1995) Journal of Vacuum Science & Technology B 13, 1810-1815.

[15] Liehr, M., Greenlief, C.M., Offenberg, M. and Kasi, S.R. (1990) Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films 8, 2960-2964.

[16] Dollet, A., de Persis, S. and Teyssandier, F. (2004) Physical Chemistry Chemical Physics 6, 1203-1212.

[17] Gates, S.M., Greenlief, C.M., Kulkarni, S.K. and Sawin, H.H. (1990) Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films 8, 2965-2969.

[18] Gates, S.M. and Kulkarni, S.K. (1992) Applied Physics Letters 60, 53-55.

[19] Flowers, M.C., Jonathan, N.B.H., Liu, Y. and Morris, A. (1993) Journal of Chemical Physics 99, 7038-7048.