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KINETIC APPROACH TO MATERIALS SYNTHESIS BY GAS-PHASE DEPOSITION

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Abstract: A survey about the synthesis of inorganic thin films through Chemical Vapor Deposition processes is presented. Particular emphasis is placed on the chemical aspects embedded in reactor fluid dynamics. The role of most important process parameters on film properties and morphology is also illustrated regarding some of the most important processes by a technological point of view. In particular, the epitaxial silicon deposition in large scale barrel reactors, the developing of a detailed chemical mechanism for the growth of InP and GaAs in horizontal MOCVD reactors, the modeling of interface roughening and of the monolayer by monolayer growth will be addressed in detail.

1. INTRODUCTION AND GENERAL ASPECTS

Gas-phase deposition is a fascinating approach to material synthesis, particularly devoted to the deposition of thin solid films [1,2]. In these processes, usually identified with the CVD acronyms (Chemical Vapor Deposition) the material is obtained from a gaseous phase by a chemical reaction involving inorganic or metalorganic precursors. The versatility of these processes allows the deposition of stable, metastable or kinetic solid products. Furthermore, different crystalline structures can be obtained as a function of the process parameters (e.g., amorphous, polycrystalline, monocrystalline, superlattice or diamond-like). Superlattices (e.g., where repeating units of distinct and well-defined phases are alternated almost at atomic scale) are of conceptual and technological importance because they permit the exploration of the differences among three-dimensional and quasi two-dimensional matter.

Some significant examples of deposition reactions involved in CVD processes are summarized in Table 1. They refer both to different deposition procedures, identified in the left column, and to different materials, such as silicon, gallium arsenide, silicon dioxide, silicon nitride and gallium aluminum arsenide. From the reported examples, it clearly appears that different precursors or their combinations can be conveniently used for the deposition of the desired material. Moreover, in the practical applications, it is possible to obtain different material features by changing the operating procedures and conditions. For example, the preparation of single crystal films is usually pursued through epitaxial deposition where the crystallographic order

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of the solid is determined by that of the substrate. The polycrystalline films are then obtained operating at reduced pressure and lower substrate temperature with respect those of the epitaxial processes above. The preparation of amorphous silicon is performed instead by operating in plasma enhanced conditions, where high deposition rates and low substrate temperature represent the typical deposition conditions. Finally, the superlattice solids are obtained through the decomposition of organometallic compounds or by mean of molecular beam epitaxy. The cited examples confirm that the control of the physical parameters such as pressure, temperature and flow rate is of particular importance [1].

SYSTEM	Energy	GLOBAL REACTION	P (KPa)	T (K)
Si Epitaxy	thermal	$\operatorname{SiH}_{4-x}\operatorname{Cl}_{x} + (4-x)/2\operatorname{H}_{2} \rightarrow \operatorname{Si} + x\operatorname{HCl} x=0,2,3,4$	10-100	1050-1450
LPCVD	thermal	$SiH_4 \rightarrow Si + 2H_2$	0.100	850-950
		$SiH_4 + N_2O \rightarrow SiO_2 + N_2$	0.100	900-1000
		$3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$	0.100	1000-1100
		$WF_6 + 3H_2 \rightarrow W + 6HF$	0.100	500-700
VPE	thermal	$12GaCl + 4AsH_3 + 2As_2 + As_4 \rightarrow 12GaAs + 12HCl$	100	800-1100
MOCVD	thermal	$Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + 3CH_4$	10-100	800-900
		$Ga(CH_3)_3 + x/2Al_2(CH_3)_6 + AsH_3 \rightarrow Al_xGa_{1-x}As + yCH_4$	10-100	800-1000
		$In(CH_3)_3 + PH_3 \rightarrow InP + 3CH_4$	10-100	600-900
PECVD	plasma	$\operatorname{SiH}_4 \xrightarrow{e^-} a - \operatorname{Si:} H + H_2$	0.100	300-600
		$SiH_4 + NH_3 \xrightarrow{e^-} SiN_xH_y + zH_2$	0.100	400-700
PCVD	photon	$SiH_4 + N_2O \xrightarrow{hv} SiO_2 + N_2$	0.1-1.0	300-600
		$In(CH_3)_3 + P(CH_3)_3 + 3H_2 \xrightarrow{hv} InP + 6CH_4$	0.1-1.0	600

Table 1: Examples of CVD processes

Obviously, such a variety of processes is performed in reactors properly designed for the desired feature. Some examples of the most common CVD reactors are illustrated in Fig. 1. All the reactors hold the wafers through a hot susceptor usually placed inside a quartz tube. They mainly differ by the energy supply system and by the temperature of the external wall (*i.e.*, hot or cold).

The horizontal reactor is a small scale deposition system usually adopted during process developing or in research conditions. Generally it is operated in cold wall conditions and at atmospheric or at reduced pressure. The prevailing fluid dynamics conditions are usually complex, leading to film thickness control problems along the reactor coordinate [3-6]. On the contrary, the high productivity is the key characteristic of barrel reactors, where 12-24 wafers per batch can be processed. The wafers are held by a slowly rotating prismatic susceptor. Also these reactors are operated in cold wall conditions and the internal gaseous fluxes are strongly influenced by the temperature gradients and by the gas inlet apparatus [7-17]. The low pressure reactors, usually adopted for polysilicon deposition, operates in hot wall conditions. Accordingly, the

fluid dynamics role on film properties control is less important than in the previously described reactors. The LPCVD reactor loads a high number of wafers (e.g., 150-300) placed vertically and orthogonally to the main gas flow. Gas flows in the annular zone surrounding the wafers and diffuse in the intrawafer region [18-22]. To contrast the precursors depletion along the reactor axial coordinate, proper gas distribution apparatus are also adopted [23,24]. The vertical reactor holds the wafers horizontally over a hot rotating susceptor while the gases are injected orthogonally to the deposition surface. This reactor is usually adopted for processing very large diameter wafers (8"-12") because the very good control of radial uniformity in film thickness. The reactor for Rapid Thermal Processes is similar to the vertical one with the exception of practically eliminating the susceptor because it is used to grow very thin films with a high turnover ratio [25-28]. Processes activated by plasma are performed in reactors where electrodes are present. Usually one of the electrodes holds also the wafers and the plasma is generated in between the two electrodes. Different flow configurations can be arranged, being the flow orthogonal or parallel to the wafers the most frequently adopted [29-32]. Particularly relevant for the growth of superlattices and the other structures at low dimensionality is the Molecular Beam Epitaxy (MBE) apparatus where the film growth is performed by the collision with the substrate of a molecular beam. The process operates at high vacuum conditions controlling the film characteristics by means of in situ spectroscopy techniques (LEED, AES, AUGER) [33]. Unfortunately, these systems are characterized by a low productivity and despite their importance they will no be addressed here.



Fig. 1. Examples of common type of CVD reactors.

A comparison between the capability of the different growth processes briefly described above with respect to the epitaxial film growth is illustrated in Table 2.

Mathematical models of the deposition reactors are of course particularly valuable both to guide the experimental researches and to design the equipments employed in material preparation. These models must include all the physical and chemical implications of the phenomena involved in the processes and schematically depicted in Fig. 2a [25,34,35]. Specifically, the growth process involves the diffusion of gaseous species towards the growing surface in a non isothermal flow field, the adsorption of the reactants and their diffusion on solid surface, the surface reactions and finally the diffusion of gaseous reaction products into the bulk gas. Depending on which of the above steps is the rate determining step of the process, the temperature dependence of film growth rate has a general behavior as that illustrated in Fig. 2b [36,37]. At low temperatures the kinetic aspects prevail, leading to a growth rate strongly dependent from temperature. At higher temperatures transport phenomena prevail and a smooth dependence of growth rate from temperature is observed.

process feature	CVD	MOCVD	MBE
growth rate (µm/min)	0.05 - 2.0	0.02 - 0.5	0.001 - 0.3
film thickness control (A)	+250	+50	+50 (easy)
			+5 (possible)
morphology	good	good	excellent
film homogeneity	excellent	good	good
doping control (cm ⁻³)	5-1014 - 1019	1015 - 1019	5.1016 - 1019
apparatus cost	average	average	high
advantages	large scale flexibility	high versatility	low temperature
disadvantages		carbon contamination	low growth rates
industrial applications	yes (largely)	yes	yes - in developing
automation	already realized	easy	possible

Table 2. Comparison of main features of different growth processes with respect to the epitaxial film growth [2].

From the previous analysis it appears that the modeling of deposition processes involves the mastering of phenomena occurring on different length scales. The situation is shown in Fig. 3, where the interconnection between the substrate scale (e.g., of the order of centimeters) and the microscopic scale (e.g., of the order ofAngstroms) is illustrated [38]. Clearly, the latter requires an analysis of the atomic details of the surface. At reactor scale, the involved phenomena belong to the domain of fluid dynamics, gas phase kinetics and transport phenomena, whose analysis can be performed through a traditional chemical engineering approach based upon continuous conservation equations. The latter scale, that involves an analysis of the elementary surface processes, requires a physical and physico-chemical approach instead. The mentioned interconnection arises from the fact that the growth rate is affected both from the rates of surface processes and from the rates at which reactive species diffuse to and from the surface. Moreover, surface chemistry affects the rate of nucleation and growth and then it can determine the deposition selectivity and the surface morphology.

The aspects mainly related to the modeling issues at wafer scale will be here addressed in sections 2 and 3, while issues inherent the physico-chemical implications will be treated in sections 4 and 5. Finally, in section 6 some significant examples of the topics theoretically developed in sections 2 and 3 will be presented. In particular, the epitaxial silicon deposition in large scale barrel reactors and the InP and GaAs growth by MOCVD will be examined.



Fig. 2 (a) Schematic of fundamental transport and reacting processes in CVD. (b) General behavior of film growth rate as a function of substrate temperature in CVD processes.



Fig. 3. Schematic of the different scales and characteristic lenghts in modeling CVD processes [38].

2. PHYSICO CHEMICAL IMPLICATIONS VERSUS FLUID DYNAMICS

Advanced material synthesis is pursued through the synergic convergence among different disciplines, such as chemistry, physics and engineering. All of them are devoted to the understanding of the existing relationships between the internal structure of the material and its properties, to the material selection, to its design and to the management of its chemical synthesis. A summary of the physical and physicochemical implications involved in material preparation is reported in Table 3, where the rows refer the different phenomena while the columns indicate the corresponding physical parameters. The last column evidences the material properties.

Subject	Material	Interfacial	Macroscopic	Restrictions
	Parameters	Quantities	Quantities	
Thermodynamics	- latent heats		- temperature	
-phase equilibria	- phase transition		- composition of	
	- temperature		the phases in	
	- free-energy excess		equilibrium	material
Nucleation	- interfacial tensions		time	
Homogeneous Phase	- reactive cross-			composition
Kinetics	sections		time	
	- rate constants			
	- diffusivities			
Interfacial &	- interfacial kinetics	- surface		
surface processes	parameters	composition		1
kinetics	-	-		
Fluid dynamics	- mixtures viscosity	- boundary	fluid velocity]
		layer		f
		thickness		material
Energy transport	- thermal	- interfacial	temperature	
	conductivity	temperature		
Crystalline Structure:			-amorphous,	structure
			-monocrystalline	
			-polycristalline	
			-eterojunctions	

Table 3. Physico-chemical parameters affecting the material properties.

In this section the attention will be focused on the simulation of reacting flow at wafer scale to simulate film growth rate and film composition. Depending by the reactor configuration and by the deposition condition the relative importance of fluid dynamics and chemistry changes as already illustrated regarding Fig. 2b. At wafer scale, the approach consists in the evaluation of flow and temperature fields and precursors' distribution within the reactor through classical conservation equations. In the conditions usually prevailing in CVD reactors, conservation equations can be written in pseudo steady state because the extremely low value encountered for growth rates with respect flow velocity (*i.e.*, relative ratio of about 10^{-6}). At this level, the

macroscopic film properties are identified by a few parameters such as substrate temperature, density and composition.

The general CVD reactor model involved the continuity, the momentum and the energy conservation equations together with the mass conservation equation for the deposition precursors [34]. Because the CVD systems usually operate in diluted conditions, the simpler Fick law for the mass flux can be adopted instead that the detailed Stefan-Maxwell equations [39-41]. Furthermore, considering the important role of the thermal diffusion effect such a contribution is included in the expression of the mass flux whenever high temperature gradients are present within the reactor [34,42]. From the side of the energy balance, due to the low conversions usually obtained in CVD reactors, the contribution of the heat of reaction and of the heat generated by viscous dissipation to the energy balance is generally neglected [41,43].

Under the hypothesis discussed above, the model equations for a generic CVD reactor are the momentum, continuity, energy and species conservation equations as reported below:

$$\rho \mathbf{v} \cdot \nabla \mathbf{v} + \nabla \mathbf{P} = \rho \mathbf{g} + \nabla \cdot \left[\mu \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^{\mathbf{T}} \right) - \frac{2}{3} \mu (\nabla \cdot \mathbf{v}) \mathbf{I} \right]$$
(1)

$$\nabla \cdot (\rho \mathbf{v}) = 0 \tag{2}$$

$$\rho C_{p} \mathbf{v} \cdot \nabla T = \nabla \cdot \left(\mathbf{k}_{T} \nabla T \right) + \sum_{k=1}^{NRG} \widetilde{\mathbf{R}}_{k}^{G} \left(-\Delta \widetilde{\mathbf{H}}_{k} \right)$$
(3)

$$\mathbf{v} \cdot \nabla(\boldsymbol{\rho}\boldsymbol{\omega}_{i}) = \nabla \cdot \left[\boldsymbol{\rho} D_{i} \left(\nabla \boldsymbol{\omega}_{i} - \boldsymbol{\alpha}_{Ti} \boldsymbol{\omega}_{i} \nabla \ln T\right)\right] + M_{i} \sum_{k=1}^{NRG} v_{ik}^{G} \widetilde{\mathbf{R}}_{k}^{G}$$
(4)

where v, g, P, T, ρ , μ , C_p, k_T and I are the velocity vector, the gravity acceleration, the system pressure, the temperature, the mass density, the viscosity, the specific heat, the thermal conductivity of the gaseous mixture and the identity matrix, respectively, while the superscript ^T identifies the and transposed vector. With reference to the *ith* specie, ω_i , D_i and α_{Ti} are the mass fraction, the effective diffusion coefficient inside the mixture and the thermodiffusion factor, respectively. Considering the usually high precursor dilution in the carrier gas, the effective diffusion coefficient can be safely approximated to the binary diffusion coefficient with respect to the carrier. The gas density has to be calculated through the equation of state for ideal gases ($\rho = PM_W / RT$) because the use of the Boussinesq approximation is not adequate in CVD systems. Furthermore, also the dependence on temperature of all the physicochemical properties present in the model must be included [26,27]. The fluid dynamics

regime usually prevailing in CVD systems is laminar [34]. Recently, reactors operating in turbulent conditions were theoretically examined [43].

The mass balance of the *ith* chemical specie (eq. (4)) includes contribution from diffusion, convection and gas phase production due to chemical reactions in gas phase. The rate and the enthalpy change of those reactions are \tilde{R}_k^G and $(-\Delta \tilde{H}_k)$, respectively. In eq. (4), the diffusion flux includes the contribution of the ordinary diffusion (*i.e.*, driven by the concentration gradients) and of the thermodiffusion, or Soret diffusion (*i.e.*, driven by thermal gradients).

The boundary conditions of the equations above (1)-(4) are specific to the reactor configuration, but some are generally adopted such as no-slip and nopenetration conditions at solid walls (*i.e.*, susceptor and outer bell-jar). Because of the incorporation and the release of atoms in correspondence of the growth interface, rigorously, a finite velocity normal to the substrate should exists. Nevertheless, in the condition usually prevailing in the deposition processes under examination such a value is so small that it can be neglected, leading again to no-slip conditions. The flow velocity at the inlet is usually specified and no-stress or fully developed flow conditions are imposed at outlet section. The thermal boundary conditions influence significantly the flow. Usually a simplified furnace, with constant susceptor and wall temperatures is considered, but in more detailed calculation proper heat flux boundary conditions can be adopted [26,27]. About the boundary condition on species mass conservation, no net flux at non reacting surfaces is the condition generally adopted. On the deposition surfaces the mass flux is equated to the net rate of incorporation due to surface chemical reactions:

$$-\rho D_{i} \mathbf{n} \cdot \left[\nabla \omega_{i} - \alpha_{Ti} \omega_{i} \nabla \ln T \right] = M_{i} \sum_{k=1}^{NRS} v_{ik}^{S} \widetilde{R}_{k}^{S}$$
(5)

where the product $v_{ik}^S \tilde{R}_k^S$ represents the rate of transformation of *ith* component due to *kth* surface reaction.

The linear growth rate of the film can then be estimated by the net incorporation rate of the NF film species:

$$G = \frac{M_s}{\rho_s} \sum_{j=1}^{NFNRS} \sum_{k=1}^{NRS} v_{jk}^S \tilde{R}_k^S$$
(6)

where M_s and ρ_s are the molecular weight and the mass density of the film, respectively.

2.1 Computational Details

In the solution of CVD reactor models, momentum and energy conservation equations are strongly coupled, while the *ith* species mass conservation equation is usually weakly coupled with the preceding ones. Accordingly, it is often possible to separate the flow problem from that of the precursor distribution within the reactor. Besides reducing storage and computational requirements, the splitting of the problem has the additional advantage of allowing the analysis of different chemical mechanisms for the same flow situation. This approximation is not valid when large density changes are associated with the deposition process [44]. The schematic sequence of computations needed to solve the simulation of a CVD reactor is here illustrated in Fig. 4.



Fig. 4. Schematic illustration of the different elements involved in solving a CVD reactors model (dilute reactants in inert carrier gas)

Because the non linear form of the CVD model equations, they have to be solved numerically, for example by means of the finite elements technique, that has the advantage to easier handle complex reactor geometry [26,27,45]. Nowadays, commercial general purpose codes are available to be used for the solution of CVD equations. We can mentioned FIDAP [46], FLUENT [47], CFX4 [48], PHOENICS-CVD [49] and MP-SALSA [50]. In particular, FIDAP and MP-SALSA are based on

the finite elements method while FLUENT, PHOENICS-CVD and CFX4 were based on the finite volumes method. All those general pourpose codes offer a reasonable capability to handle complex flow simulations in a 2D geometry, while to treat the fully 3D calculations a great amount of computer time is still required. In fact, in such an approach, the solution of the general 3D problem with arbitrary kinetics involving arbitrary number of chemical species is limited by the memory and the speed of the current computer generation. 2D models with large kinetics mechanism or 3D models, in transport limiting conditions and moderately complex geometry represent the limits of the current modeling complexity. Considering the dramatic growth trend of computer capability, such a limit will no last longer. For example, MP-SALSA is a multi parallel code already designed to handle non stationary 3D multicomponent CVD reactor, where on the machines today available, the simulation of the full problem involving not symmetric flows takes almost one week.

Besides the computational difficulties, the main problem arising the simulation of CVD reactors is related to the estimation of the models' parameters. The estimation of thermodynamics (*e.g.*, enthalpy and heat capacity) and transport parameters (*e.g.*, viscosity, thermal conductivity and diffusivity) is easier than the estimation of the kinetic ones (*e.g.*, reaction rate parameters). For this reason, a chapter will address specifically the latter issue. Regarding the transport parameters, they can be estimated with consolidated relationships derived from the molecular theory of gases as a function of Lennard-Jones parameters [39,51,52].

2.2 One Dimensional Approach to Horizontal Reactor

Considering the computational complexities discussed above, when the system geometry is not very complicated, such as in the case of horizontal reactors or in vertical spinning reactors, a first approximation analysis can be performed using monodimensional models. These models can describe the system only along the reactor main coordinate with a quite satisfactory approximation if proper relationships to describe the precursors mass transport towards the susceptor are adopted. Here, such an approach will be described with reference to a horizontal reactor, but similar descriptions can be found also for vertical reactors (e.g., imprinjing jet and rotating disk configurations [53,54]) and for barrel reactors [12]. Those models allow to analyze rapidly the reactors features and optimizations, specially when systems involving complex kinetics are considered (e.g., MOCVD processes).

The model equations can be derived directly from the complete set of equations discussed above. In particular, the model reduces to mass and energy balance equations, while those defining the reactor fluid dynamics are omitted. The last information is obtained introducing suitable relationships usually based on the boundary layer theory or on fully developed flow situations.

The mass balance of each gaseous specie, except the carrier, and the overall one could then be written as follows:

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$$\frac{d(F\omega_i)}{dV} = M_i \sum_{k=1}^{NRG} v_{ik}^G \widetilde{R}_k^G - S_v N_i \qquad i=1, NCG-1$$
(7)

$$\frac{\mathrm{dF}}{\mathrm{dV}} = -\mathrm{S}_{\mathrm{v}} \sum_{i=1}^{\mathrm{NCG}} \mathrm{N}_{i} \tag{8}$$

where $F = v\rho\Omega$, V, S_v are the overall mass flow rate, the reactor volume and the deposition surface per unit reactor volume, respectively, being the other symbols already defined. For the case of a horizontal reactor, the differential volume is proportional to the reactor coordinate z by the reactor free cross section Ω , (*e.g.*, $dV = \Omega dz$). As usual, the superscripts "G" and "S" indicate a quantity referred to the gas phase and to the deposition surface, respectively. The mass flux includes the contribution of the ordinary and of the Soret diffusion, and in a 1D schematization can be written as follows [12,35,55]:

$$N_{i} = k_{ci} \rho \left[\left(\omega_{i} - \omega_{i}^{s} \right) - \alpha_{Ti} \omega_{i} \left(1 - \omega_{i} \right) \ln(T_{S}/T_{G}) \right]$$
(9)

where k_{ci} , T_S and T_G are the mass transfer coefficient, the susceptor and gas temperatures, respectively. The second term in eq. (9) was derived assuming a linear variation of the temperature within the boundary layer. The mass transfer coefficient k_{ci} can be evaluated with reference to the gas motion within a rectangular duct by means of a relationship derived in the framework of boundary layer theory [56]:

$$\frac{\mathbf{k}_{\rm ci}\mathbf{H}}{D_{\rm i}} = \mathrm{Sh} = \left[\frac{1}{\mathrm{Sh}^{\infty}} + 0.25\sum_{j=1}^{\infty}\gamma_{j}\exp\left(-\frac{8\beta_{j}^{2}z}{3\mathrm{H\,Re\,Sc}}\right)\right]$$
(10)

being Sh^{∞} the limiting value for fully developed flow [57,58] and H, z, Re and Sc the reactor spacing between the susceptor and the external wall, the longitudinal coordinate, the Reynolds (evaluated with respect to H) and the Schmidt dimensionless numbers, respectively, while γ_j and β_j are the numerical parameters of the serie [57]. Then, the surface weight fractions ω_i^S can be obtained equating the mass flux towards the deposition surface with the corresponding surface reaction rate:

$$-N_{i} = M_{i} \sum_{j=1}^{NRS} v_{ij}^{S} \widetilde{R}_{j}^{S} \qquad i=1, NCG-1$$
(11)

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being the carrier gas phase and surface weight fractions calculated by means of the consistency equations ($\sum_i \omega_i = \sum_i \omega_i^S = 1$). The adsorbed species concentrations can be calculated imposing their no net production:

$$\sum_{j=1}^{\text{NRS}} \mathbf{v}_{ij}^{\text{S}} \widetilde{\mathbf{R}}_{j}^{\text{S}} = 0 \qquad \qquad i=1,\text{NA}$$
(12)

About the energy balance, the following equation can be directly derived from eq. (3):

$$\frac{d(FC_pT_G)}{dV} = S_v h_s (T_S - T_G) - S_e U (T_G - T_C) + \sum_{k=1}^{NRG} \tilde{R}_k^G (-\Delta \tilde{H}_k)$$
(13)

where T_C , S_e , h_s and U are the cooling gas temperature, the external tube surface per unit reactor volume, the heat transfer coefficient at susceptor surface and the overall one with respect to the heat transfer outside the reactor, respectively. The heat transport coefficients can be evaluated through relationships similar to eq. (10), as those reported in [12]. The heat of reaction contribution in eq. (13) can be safely neglected because the low precursors conversions and the high dilution usually prevailing in the considered systems. The solution of the algebraic and ordinary differential equations system can be pursued by means of the SDASPK subroutine [59], adopting $\omega_i = \omega_i^\circ$, $F = F^\circ$ and $T_G = T_G^\circ$ as initial conditions associated to eqs. (7), (8) and (13), respectively.

3. REACTION KINETICS

As it has been already stressed, the solution of balance equations together with the evaluation of the growth rate of the solid implies the knowledge of a detailed reaction scheme for both gas and surface chemistry. Moreover, the specific expressions of the involved reaction rates must be known. Accordingly, the definition of a complete reaction pathway is still the more complex problem to be solved in modeling a CVD system.

The developing of a detailed kinetic mechanism is still a challenging task mainly for two reasons: the selection of the most significant pathway and then the estimation of all the involved reaction rate parameters. A comprehensive procedure to obtain a detailed kinetic scheme can be found in [60]. After the development of the most detailed kinetic scheme and of a fast estimation of the involved parameters, a sensitivity analysis can be performed to reduce the mechanism to the essential pathway. At this point, a great effort must be placed in the determination of the reaction rate parameters of the most important reactions. A kinetic scheme for such as a heterogeneous process as CVD must be composed by two different sub-schemes, one dealing with the gas phase chemistry and the other with the surface one.

The rate of the *kth* gas phase reaction can be expressed as follows:

$$\widetilde{\mathbf{R}}_{k}^{G} = k_{k} \prod_{i=1}^{NC} C_{i}^{q_{ik}^{G}} \left(1 - e^{\Delta G_{k}/RT} \right)$$
(14)

where k_k is the reaction rate constant and q_{ik}^G is the reaction order with respect to the *i*th species, whose molar concentration is $C_i = \omega_i \rho / M_i$. Finally:

$$\Delta G_{k} = \Delta G_{k}^{0} + RT \ln \prod_{i=1}^{NC} (C_{i}RT)^{\nu_{ik}^{G}}$$
(15)

is the free energy change associated to the kth reaction. In the formulation of eq. (15), an ideal gas at atmospheric pressure is considered for reference state.

The gas phase mechanism involves different molecular species and their fragments. Its analysis can be accomplished through the methods of the gas phase chemical kinetics and it will not more specifically discuss here. It is important to remark that in many cases CVD reactors operate at reduced pressure and thus many reaction rate must be considered in their "fall-off " region [61]. Nowadays, the *a priori* estimation of rate constants for gas phase reactions starts to be possible by means of the transition state theory coupled with suitable *ab initio* softwares to perform quantum-mechanics calculations. Among all the code available, we can mention G94 [62] and AMPAC [63]. More rough estimations can be performed through the methods illustrated in [64,65].

The kinds of reactions that can occur at the growing surface are mainly of three types: adsorption, surface recombination and desorption. A general formulation suitable for all the three mentioned cases is the following:

$$\widetilde{\mathbf{R}}_{k}^{S} = \mathbf{k}_{k}^{S} \left(\prod_{i=1}^{NC} (C_{i})^{q_{ik}^{S}} \right)^{NSITE} \prod_{m=1}^{NCA_{m}} \left(C_{im}^{S} \right)^{p_{ik}}$$
(16)

being C_{im}^{S} the concentration of the adsorbed *ith* specie over the *mth* kind of surface site. In particular, $C_{im}^{S} = \Psi_m \theta_{mi}$, being Ψ_m and θ_{mi} the surface concentration of *mth* kind of surface site and the coverage fraction of *ith* specie on the *mth* site, respectively. k_k^{S} and p_{ik} are the surface reaction rate constant and the reaction order with respect *ith* adsorbed specie, respectively. Eq. (16) reflects that the rate of a surface reaction depend on the probability of a gas phase specie to stick on a free surface site or to interact with one or more adsorbed species. The above formulation considers different types of surface sites on which the interaction can take places. This aspect is particularly important when the growth of semiconductor compounds is examined.

The adsorption rate can be expressed through the frequency of the collision of the molecules coming from gas phase on the surface, times both the sticking coefficient and the probability to find an empty surface site. On the whole, the rate constant to be used together with eq. (16) comes out as follows:

$$k_{k}^{S} = \gamma_{k} \sqrt{\frac{RT}{2\pi M_{k}}} e^{-E_{k}/RT} \left(\prod_{m=1}^{NSITE} \prod_{i=1}^{NCA_{m}} \psi_{m}^{-p_{ik}} \right)$$
(17)

where γ_k is the steric factor for adsorption of *kth* specie and E_k the activation energy of the process. As well as the rate constants of surface processes, they depend on the specific details of the interactions of adsorbed molecules with surface atoms. If $\gamma_k = 1$ and $E_k = 0$, eq. (17) gives the maximum possible adsorption rate. Unfortunately, such a limit can not be established for surface recombination and desorption reactions. In such cases, experimental information about surface bond frequency and strength are often used. If such information is not available, values corresponding to usual intervals are often adopted to obtain first approximation data.

A couple of examples of deposition mechanism based only on elementary reactions are illustrated in Figs. 5 and 6 where the sketch of indium phosphide and silicon epitaxial deposition are briefly illustrated. In those examples, InP is grown using metal-organic precursors (*e.g.*, trimethylindium and phosphine), while silicon is grown from silane. The rate constants of the two mechanisms are summarized in Tables 4 and 5.



Fig. 5. (a) Schematic of Silane decomposition pathways [66-72].

Table 4. Chemical mechanism for silicon deposition from SiH₄. $k = AT^m P^n \exp(-E / RT)$, units consistent with mol, cm, s, cal, K and atm. e = estimated through thermochemical methods [64,65]. c = collisional theory (eq. 17). \$ = surface site. Values interpolated on the high and the low pressure values reported in the cited references (range 1 mTorr - 1 Torr). f = forward reaction, b = backward reaction.

	Reaction	log ₁₀ A	m	n	E	ref.
G1	$SiH_4 \leftrightarrow SiH_2 + H_2$	27.41	-4.46	0.994	57241	66
G2f	$H_3SiSiH + H_2 \rightarrow SiH_2 + SiH_4$	13.97	-	-	4092	66
G2b	$SiH_2 + SiH_4 \rightarrow H_3SiSiH + H_2$	10.98	1.10	-	5790	66
G3f	$H_3SiSiH + SiH_4 \rightarrow Si_2H_6 + SiH_2$	14.24	0.40	-	8899	66
G3b	$Si_2H_6 + SiH_2 \rightarrow H_3SiSiH + SiH_4$	14.24	0.20	-	8473	66
G4	H3SiSiH ↔ SiH4 + Si	40.50	-8.43	0.999	61001	66
G5	$Si + Si_2H_6 \leftrightarrow SiH_2 + H_3SiSiH$	15.11	-	-	12600	66
G6	H ₃ SiSiH ↔ H ₂ SiSiH ₂	31.11	-6.76	0.997	9153	66
G7	Si ₂ H ₆ ↔ H ₃ SiSiH + H ₂	42.36	-8.77	1.004	58970	66
G8	$Si_2H6 \leftrightarrow SiH4 + H2$	52.39	-11.6	0.993	57706	66
G9	$2H + M \leftrightarrow H_2 + M$	17.20	-0.60	-	-	67
G10	$SiH_4 + H \leftrightarrow SiH_3 + H_2$	14.00	-	-	2500	68
S1	$SiH_4 + 2\$ \rightarrow SiH_3^* + H^*$	19.06	0.5		3000	69,70
S2	$SiH_3^* + \$ \rightarrow SiH_2^* + H^*$	17.64	-		27000	69,70
S 3	$2 \operatorname{SiH}_2^* \to 2 \operatorname{SiH}^* + H2$	24.38	-		45000	e, 69,70
S4	$Si + \$ \rightarrow Si^*$	11.77	0.5		0	e,c
S5	$SiH + \$ \rightarrow SiH^*$	11.77	0.5		0	e,c
S6	$Si^* \rightarrow Si(s) + $	20.90	-		44000	
S 7	$SiH_2 + \$ \rightarrow SiH_2^*$	11.76	0.5		0	e,c
S8	$H + \$ \rightarrow H^*$	12.63	0.5		0	с
S9	$SiH_3 + \$ \rightarrow SiH_3^*$	11.76	0.5		0	e,c
S10	$Si_2H_2 + 2 $ $\Rightarrow 2 SiH^*$	20.56	0.5	•	3000	e,c
S1 1	$SiH^* \rightarrow Si(s) + \frac{1}{2}H_2 + $	11.90	-		47000	70
S12	$2 \text{ H}^* \rightarrow \text{H}_2 + 2 $	22.11	-		47000	70

Because its industrial importance, gas phase and surface chemistry of silane were extensively studied in the literature and presently the overall growth mechanism is almost consolidated [66-72]. The mechanism was derived by means of theoretical and experimental analysis. Particular effort was devoted to the experimental determination of the species adsorbed on the surface and to the corresponding reaction rate values. Unfortunately, the same level of reliability on the chemical mechanism data is not available for other silicon precursors (e.g., chlorosilanes) and the studies on the surface mechanism are still under progress.



Fig. 6. Gas phase and surface reaction involved in InP epitaxial deposition. In and P containing species stick only on opposite atom site, methyl and hydrogen stick on both kind of sites [55,73].

Table 5. Chemical mechanism for InP deposition from InMe₃ and PH₃. $k = AT^mP^n \exp(-E / RT)$, units consistent with mol, cm, s, cal, K and atm Symbols: Me = CH₃. e = estimated through thermochemical methods [64,65]. c = collisional theory (eq. 17). p_p and i: In and P terminated surface sites, being each surface concentration $\Psi = 0.7 \cdot 10^{-9} \text{ mol/cm}^2$

	Reaction	log ₁₀ A	m	n	E	ref.
G-1	$InMe_3 \leftrightarrow InMe + 2Me$	15.720	0.0	-	47200.	а
S-1	$\ln + \$_n \rightarrow \ln^*$	11.452	0.5	-	0.	с
S-2	$InMe + \$_p \rightarrow InMe^*$	11.452	0.5		0.	с
S-3	$InMe_3 + \$_i + \$_p \rightarrow InMe^* + Me_i^* + Me$	20.793	0.5	-	0.	с
S-4	$InMe_3 + 2\$_p \rightarrow InMe^* + Me_p^* + Me$	20.793	0.5	-	0.	с
S-5	$PH_3 + 2\$_i \rightarrow PH_2^* + H_i^*$	21.129	0.5	-	0.	с
S-6	$PH_3 + \$_i + \$_p \rightarrow PH_2^* + H_p^*$	21.129	0.5	_	0.	c
S-7	$InMe^* + \$_i \rightarrow In^* + Me_i^*$	17.000	0.0	-	0.	e
S-8	$\mathbf{PH}_{2}^{*} + \mathbf{In}^{*} \rightarrow \mathbf{InP}_{\mathrm{sol}} + \mathbf{H}_{2} + \mathbf{\$}_{i} + \mathbf{\$}_{p}$	17.000	0.0		0.	e
S-9	$2H_i^* \rightarrow H_2 + 2\$_i$	17.000	0.0	-	10000.	e, des
S-10	$2H_p^* \rightarrow H_2 + 2\$_p$	17.800	0.0	-	27000.	e, des
S-11	$Me_i^* \rightarrow Me + \$_i$	12.000	0.0	-	30000.	e, des
S-12	$Me_p^* \rightarrow Me + \$_p$	12.000	0.0	-	30000.	e, des
S-13	$\operatorname{In}^* \to \operatorname{In} + \$_i$	12.204	0.0	-	53500.	74 des
S-14	$Me_i^* + H_i^* \rightarrow CH_4 + 2\$_i$	17.000	0.0	-	10000.	e, des
S-15	$Me_{p}^{*} + H_{p}^{*} \rightarrow CH_{4} + 2\$_{p}$	17.000	0.0	-	25000.	e, des
S-16	$PH_2^* + H_p^* \rightarrow PH_3 + \$_i + \$_p$	17.000	0.0	-	30000.	e, des
S-17	$PH_2^* + H_i^* \rightarrow PH_3 + 2\$_i$	17.000	0.0	-	20000.	e, des
S-18	$InMe^* \rightarrow InMe + \$_p$	14.000	0.0	-	42000.	73 des

The derivation of the detailed chemical mechanism for InP and other semiconductor compounds, mainly grown through MOCVD processes, is usually more complex because the great amount of radical fragments generated by the precursor decomposition [55,74]. Furthermore, because the great number of different

organometallic precursors that can be used for the same film deposition, a lower amount of experiments per kind of precursor is performed to deepen the overall mechanism.

Besides the fact that the two reported mechanisms are speculative in some aspects, they allow the simulation of the epitaxial growth of both considered materials by means of the already described approach. The knowledge of the detailed chemical mechanism is important also in depositions performed when the mass transport is the rate determining step of the process. In fact, information about the film composition and more important on dopant incorporation can be obtained only from the knowledge of a reliable chemical pathway.

4. INFLUENCE OF SOLID-PHASE DYNAMICS ON SURFACE CHARACTERISTICS

A deposition process has to produce materials with reproducible properties such as purity, controlled composition, microstructure, surface morphology [1,38]. As already mentioned in the preceding sections, the control of material quality depends strongly on external variables that affect the deposition steps, such as substrate temperature, gas feed composition, pressure and gas flow rate. Consequently, an important problem is to state how the rate of each of them affects the overall growth rate and how the relative rates of the various surface processes could determine the surface structure and morphology. Such processes include surface decomposition, lateral diffusion, nucleation and atomic insertion on a kink [75].

The influence of chemical kinetics on surface morphology can be experimentally recognized by means of sensitive techniques such as the Auger spectroscopy and the Scanning Tunneling Microscopy. Wide investigations have been made on the dependence of surface morphology on the incident flux of the deposition precursors onto the growing surface, because the collision probability among diffusing atoms increases proportionally to the flux value F. The formation of islands on the top of other islands can be observed, leading to the growth of a rough surface with irregular shape. At high fluxes and low temperatures, the stochastic addition of atoms with no lateral transport yields a completely random surface. In this case, the surface roughening during growth can be simulated through the ballistic deposition model illustrated in Fig. 7a [76,77]. In such a framework, the species stick on the first nearest site they encountered on the growing surface. Actually, such a situation is not altogether realistic since the lateral transport of atoms always flattens the surface.

With reference to a two dimensional substrate, whose local coordinate is \mathbf{x} , to describe the time evolution of the system, a surface coordinate $h(\mathbf{x},t)$, representing the local film thickness at time t and at any position \mathbf{x} , can be adopted as illustrated in Fig. 7b. The roughness of the growing surface can be then expressed as follows [75-77]:

$$\sigma(\mathbf{L}, \mathbf{t}) = \sqrt{\frac{1}{L} \int_{0}^{L} \left[\mathbf{h}(\mathbf{x}) - \overline{\mathbf{h}} \right]^{2} d\mathbf{x}}$$
(18)

 σ represents the average difference among the local and the mean film thickness value \overline{h} , divided by the linear size of the system L. Accordingly, the kinetics of the growing surface must also describe the temporal behavior of surface rougheness σ . The concept of topographic scaling can be advantageously employed, being the surface assimilated to a fractal object that is rescaled through an anisotropic transformation. A special subclass of fractals described by a single valued function is of interest. Then, the local surface coordinate can be represented as follows [75]:

 $\mathbf{h}(\mathbf{x}) \approx \mathbf{b}^{-\boldsymbol{\chi}} \mathbf{h}(\mathbf{b}\mathbf{x}) \tag{19}$

where the exponent χ (*i.e.*, the *self affine coefficient*) gives a quantitative measurement of the *roughness* of the function h(**x**). The previous equation states that a self-affine function is rescaled in a different way horizontally and vertically: if the function is "blown-up" horizontally by a factor b**x**, correspondently it must "blow-up" verticaly by a factor b^{χ} [75]. Of course if $\chi = 1$ the transformation is isotropic and the systems is self-similar.



Fig. 7. (a) Schematic of surface roughness as a function of growth parameters. High temperature and low flux: regular growth. Low temperature and high flux: stocastic growth. (b) Schematic representation of surface geometry for roughness description.

Experimental analysis reveals that there are two different scaling regimes defined as follows:

$$\sigma(L,t) \propto t^{\beta} \qquad t < t_{x} \tag{20a}$$

$$t_x \propto L^2$$
 (20b)

$$\sigma(L) \propto L^{\alpha} \qquad t > t_{\chi} \tag{20c}$$

The involved parameters are called *scaling exponents*, and particularly α , β and z are the roughness, the growth and the dynamic exponents, respectively. They are not independent one from the other and an important problem is their prediction by means of a theoretical approach to surface dynamics.

Several attempts have been performed to formulate continuous dynamic equations able to describe the evolution of the growing surface by taking into account the competition between a stochastic roughening and the smoothing mechanisms. A general differential equation describing the variation with time of the interface height at any position can be written as:

$$\frac{\partial \mathbf{h}(\mathbf{x},t)}{\partial t} = -\mathbf{K}\nabla^{4}\mathbf{h} + \lambda\nabla^{2}(\nabla\mathbf{h})^{2} + \mathbf{F} + \eta(\mathbf{x},t)$$
(21)

The first term in the r.h.s. accounts for the surface diffusion of the deposited particles where the motion of an atom mainly depends in the number of bonds that must be broken for diffusion to take place. Since they increase with the local curvature of the surface, the driving force of the diffusion process is proportional to $-\nabla^4 h$. The second term represents the simplest non linear expression to describe the erosion of hills and the filling of valleys that is consistent with matter continuity and translational invariance [78]. $\eta(\mathbf{x}, t)$ is a thermal noise term reflecting the influence of the random fluctuations that has the following properties:

$$\overline{\eta(\mathbf{x},\mathbf{t})} = 0 \tag{22a}$$

$$\overline{\eta(\mathbf{x},t)\cdot\eta(\mathbf{x}',t')} = 2\mathrm{D}\delta(\mathbf{x}-\mathbf{x}')\cdot\delta(t-t')$$
(22b)

where D and $\delta(...)$ are the strength of the noise and the Dirac function, respectively. Such equations imply that the stocastic noise has no correlation in space and time since $\eta = 0$ except for the special case where t = t' and x = x'. These conditions are automatically satisfied if the variable η has the form of the Gaussian distribution [79]. The non linear eq. (21), where randomly forced fluctuations are present, cannot be analytically solved. Nevertheless, its features can be evidenced by means of the dynamic Renormalization Group method [80]. In such a framework, the scaling exponents are extracted by the *flow equations* that are obtained by submitting the system to a set of transformations where the system is examined at different length scales. Those equations describe the evolution of the parameters K and λ towards a fixed point, corresponding to an invariant situation that does not change anymore. For a two dimensional interface embedded in a three dimensional space, the following values for the scaling exponents are then obtained: $\alpha = 0.67$, $\beta = 0.20$ and z = 3.33.

Many experiments have been performed to check the validity of the mentioned scaling approach. Experimental values of α and β parameters are reported in Table 3 for the deposition of some metals. It is interesting to observe that most of the experimental values of α are in agreement with the ones predicted by equation (21).

On the contrary, for the growth of semiconductor surfaces such as silicon, the experimental values of α results close to zero. This finding reveals that the continuous eq. (21) is not altogether universal.

Table 3. Experimental roughness parameters for various metals

system	α	β
Fe	0.79	0.22
Au	0.73	-
Pt	0.68	-
Au (sputtered)	-	0.40

To deepening this aspect, it must be recalled that the lowest energy state of the crystal is consistent with the flat surface, while fluctuations break bonds and displace atoms by increasing the surface area and its energy. If v is the specific surface energy, the total surface energy H can be expressed as follows (if $|\nabla h| << 1$):

$$\boldsymbol{H}(L) \approx \nu L^2 + \frac{1}{2} \int (\nabla \mathbf{h})^2 d^2 x$$
(23)

Actually, this equation is consistent with a continuous description of the surface while the height of the crystal is discrete with jumps equal to the lattice constant a_0 . To account this fact eq. (23) can be modified as:

$$\boldsymbol{H}(\mathbf{h}) \approx \nu \mathbf{L}^2 + \int \left[0.5\nu (\nabla \mathbf{h})^2 - \boldsymbol{\varphi}_0 \cos(2\pi \mathbf{h}/\mathbf{a}_0) \right] d^2 \mathbf{x}$$
(24)

where the added term mimes the periodicity of the lattice potential energy.

The equilibrium behavior of the surface can be still examined by means of the Renormalization Group method, where the partition function Z takes the place of the dynamic eq. (21):

$$Z = \int \boldsymbol{D} h e^{-\boldsymbol{H}(h)/k_{B}T}$$
(25)

The following flow equations are obtained:

$$\frac{\mathrm{d}Y}{\mathrm{d}\ell} = 2Y\frac{X-1}{X} \tag{26a}$$

$$\frac{\mathrm{d}X}{\mathrm{d}\ell} \approx 0.199 \frac{\mathrm{Y}^2}{\mathrm{X}} \tag{26b}$$

where $X = 2\nu a_0^2 / \pi k_B T$ and $Y = 4\pi \phi_0 / \Lambda^2 k_B T$, and $\ell = \ln b$, being b a scaling parameter such as $h \rightarrow bh$.

Eq. (26a) has a fixed point for X = 1; it follows that a critical, or roughening temperature, is obtained:

$$T_{\rm R} = \frac{2\nu a_0^2}{\pi k_{\rm B}} \tag{27}$$

which separates two thermodynamically different phases as shown in Fig. 8. Then it follows that:

- if $T > T_R$, Y decreases to zero and the lattice potential vanishes, being its values proportional to Y. In this case the roughening effect prevails and eq. (21) accounts for the system dynamic.
- if $T < T_R$, Y diverges. The lattice potential prevails and then the interface has the regular structure of a crystal cut.

The latter situation includes the monolayer by monolayer growth that is also called Franck-van der Merwe growth mechanism [82]. In it, the adsorbed species diffuse over the substrate surface up to the edge where they are incorporated in the growing film. This growth mechanism is active in the epitaxial growth of semiconductors that have a thermodynamically stable surface as a consequence of the relatively high value of the parameter v. For instance, on the basis of the known values of v, it is easy to verify that for silicon the roughening temperature is very high (*e.g.*, higher than its melting temperature).

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Fig. 8. Flow diagram near the roughening transition, (from ref. [75,81]). The separatrix caming to and starting from X = 1 delimits the two phases: one for $T < T_R$ and the other for $T > T_R$.

5. ATOMIC SCALE: ROLE OF SURFACE KINETICS IN INTERFACES GROWTH

In the monolayer by monolayer epitaxial growth the classical mechanism based on terrace-ledge-kink model is particularly profitable [83]. A closed packed surface is constituted by a stepped surface of terraces as the one illustrated in Fig. 9. In the considered framework, two principal kinetic processes can take place [84]. The former is the atomic motion of adsorbed atoms on flat terraces and their interaction with steps, including their sticking in correspondence of the terrace step. In this case, crystal growth depends essentially on the existence of kinks in the steps where the atomic insertion occurs. The prevalence of this step-flow is a prerequisite to produce films of better crystallinity. An important feature is then the presence of clusters due to the aggregation of adatoms far from the terrace step. Their density is of paramount relevance in the structure homogeneity of the obtained material since the interaction of the laterally moving steps with such clusters could generate surface defects. If the cluster concentration is high a polycrystal can then be formed.

If the thermodynamic approach is applied to the formation of bidimensional clusters, and particularly to the determination of their size, the following expression for the dimension of the critical nuclei radius r^* can be obtained [85]:

$$r^* = \frac{a_0 T_m}{4(T_m - T)}$$
(28)

being a_0 the interatomic distance in the crystal lattice and T_m the melting temperature

(e.g., $a_0 = 4.08$ A and $T_m = 1410$ °C for silicon). Eq. (28) was derived assuming the molar free energy variation associated to the melting expressed as $\Delta \tilde{G}_m = \Delta \tilde{H}_m (1 - T / T_m)$. If eq. (28) is applied to silicon growth at 1000°C a critical cluster radius $r^* = 3.37$ A is obtained. This unreasonable small value evidences the inadequacy of a simple thermodynamic treatment and leads to approach the problem through the kinetic theory of nucleation.

In a CVD process, an additional source of complexity is due to the presence of surface and gas phase reactions. Except for few cases, the reaction pathways involving the deposition precursors are not usually known. Generally, some hypothesis can be done but the decomposition pathway can also strongly depend on the operating conditions. For this reason, the chemistry of the precursors must be deepened before the studies inherent the formation of surfaces.

In a strictly theoretical approach, the occurrence of surface reactions can be pursued by means of quantum mechanics. In that case, the energetic of all the possible elementary surface processes is investigated by the solution of the Schrödinger equation for the many electrons molecular systems, in the framework of the Born-Oppheneimer approximation [85-89]. The above *a priori* approach is computer time consuming, because it implies the onerous analysis of elementary steps that could eventually results of less importance. In any case, the today availability of reliable quantum mechanics codes is expected to be a breakthrough in the investigation of elementary chemical reactions [62,63].

An alternative strategy is the use of semi-empirical methods, where the experimental values of bond energies, bond lengths and frequencies of molecular vibrations are adopted to evaluate the energy of different bonding configurations corresponding to adsorbed states. Furthermore, the use of the bond order-bond length relation yields to approximate expressions of the potential energy profiles associated with the bond-breaking and bond-making processes [61,65]. It follows that the activation energy values required for the investigation of the surface events become available. Statistical mechanics and transition state theory allow the estimation of the frequency factors of the reactions. In this framework, some hypotheses about the structure of the activated complexes have to be devised, but the analogies with the exiting gas phase molecules are helpful. Of course, this latter strategy implies a heuristic aptitude in the use of experimental information coming from different sources, and sometimes chemical insight and intuition in recognizing the surface species that could play a dominant role in the reaction pathway are required.

To clarify the role of the different rate steps mentioned above, the kinetics of the thermally activated growth, at low pressure, of silicon from silane on a Si (100) surface can be examined [90,91]. A sketch of the main silane decomposition steps was already illustrated in Figure 5, being the rate constant of the involved reactions summarized in Table 4. Regarding the final aim to analyze the surface formation, a simplified lumped kinetic scheme can be considered:

$$\operatorname{SiH}_{4(g)} + 2\$ \rightarrow \operatorname{SiH}_{3}^{*} + \operatorname{H}^{*} \rightarrow \cdots \rightarrow \operatorname{Si}_{(\operatorname{ada})} + 2\operatorname{H}_{2}$$

The dots indicate intermediate reactions assumed to be fast while the superscript * indicates the adsorbed species. The adsorbed silicon atom Si_(ada) can be assumed the most abundant surface species, that diffuses and contributes to the film growth. In such an approximation, the rate of chemisorption process is equal to the flux of silane towards the growing clean surface. A kinetic model that considered both the insertion of adatoms in the step edge and the surface clusters formation through the so called Ostwald ripening can be then formulated with the aim to devise a *toy model* able to yield information on surface homogeneity [85]. A sketch of the considered mechanism is illustrated in Fig. 10. Accordingly with the Burton-Cabrera-Franck mechanism [83], the surface terraces are generated by a screw dislocation, as sketched in Fig. 11, and their width can be evaluated as $\lambda = \pi a_0 T_m / (T_m - T)$.

In the considered framework, the conservation of $Si_{(ada)}$, if its evaporation is reasonably neglected, is stated by the following equations, where only single atoms migrate over the surface, while clusters are assumed to remain steady:

$$\frac{\partial N_1}{\partial t} = R\left(\underbrace{C_{\text{SiH}_4}, N_1, N_2 \cdots}_{\text{surface reaction}}\right) - \underbrace{k_1 N_1^2}_{\text{formation}} - \underbrace{N_1 \sum_{s \ge 2} k_s N_s}_{\text{clusters growth}} - D \frac{\partial^2 N_1}{\partial x^2}_{\substack{\text{surface diffusion}}}$$
(29)

$$\frac{\partial N_s}{\partial t} = N_1 (k_{s-1} N_{s-1} - k_s N_s) \qquad s = 2, s_m$$
(30)

where $N_{1,2...}$ are the surface concentrations of single adatom, couples and clusters respectively. *D* is the surface diffusion coefficient for adatom and k_s is the rate constant of the capture of one single atom by a *s*-atoms cluster. Finally, R is the rate of silane surface decomposition, that can be expressed through eq. (17). The corresponding boundary conditions are:

$$N_1(0) = N_1(\lambda) \tag{31a}$$

$$-D\frac{\mathrm{dN}_{\mathrm{I}}}{\mathrm{dx}}\Big|_{\mathrm{0}} = \mathrm{R}_{\mathrm{in}} \tag{31b}$$

being λ the edge spacing and R_{in} the rate of insertion of a diffusing atom at step

edge. The former expression reflects the symmetric distribution of adsorbed silicon atoms on the terrace. The latter expresses instead the rate of insertion of an adsorbed atom in a terrace step. Furthermore, in agreement with the kinetic theory of nucleation, the coagulation constant k_s can be placed equal to [92]:

$$k_s \approx Ds^p$$
 (32)

where the exponent p, for circular clusters, is equal to 0.5.

The estimation of the rate of decomposition of silane implies both the identification of the surface sites and the formulation of reliable hypothesis on the structural and energetic characteristics of the species involved in the reaction. On the Si (100) surface the total concentration of silicon atoms Ψ is equal to 6.8×10^{14} atoms/cm², where each atom has a dangling bond pointing perpendicularly to the surface. The dissociation process starts by the interaction of the silane molecule with the mentioned dangling bond. The reaction rate, in agreement with the dual site dissociative mechanism of silane discussed above:

$$R = kC_{SiH_4} (\Psi \theta_v)^2 = k\Psi^2 C_{SiH_4} \left(N_t - N_1 - \sum_{s \ge 2} sN_s \right)^2$$
(33)

where the rate constant k is calculated consistently with eq. (17).

The energetic perspective of the surface by moving along an axis perpendicular to the edge, is reported in Fig. 12, where a_0 is the reticular distance while E_k is the energy of a silicon atom in a kink position. The surface diffusion is an activated process that occurs be through hops of an adsorbed silicon atom between two surface atoms.

The straightforward application of the transition state theory yields the following expression of the surface diffusion coefficient:

$$D = v_f a_0^2 e^{-E_d/RT}$$
(34)

being $v_f = 7.5 \times 10^{13} \text{ s}^{-1}$ the vibration frequency of silicon atoms and E_d the activation energy of the process. This value can be estimated from the Si-Si bond energy value (*e.g.*, 42.2 kcal/mol), leading to the reasonable approximation $E_d \cong 22$ kcal / mol. The boundary conditions (31b) can instead be rewritten as:

$$-D\frac{dN_1}{dx}\Big|_0 = a_0 v_f N_1(0) e^{-E_{in}/RT}$$
(35)

where E_{in} is the activation energy of the adatom insertion in the terrace kink, as illustrated in Fig. 12. E_{in} value is reasonably close (but lower) to the activation energy of adatom surface migration.



Fig. 9. Representation of step growth mechanism for silicon. Adsorbed surface species formation in agreement with Fig. 4.





Fig. 10. Surface atoms migration by the Otswald ripening mechanism



Fig. 11. Image of growing surface through a screw dislocation. λ terrace width.

Fig. 12. Energetic prospective of surface moving along the terrace.

The described model allows the identification of two dimensionless parameters, that are:

$$\xi = \frac{\text{rate of insertion in a step}}{\text{rate of insertion in a cluster}} = \frac{4e^{(E_d - E_{in})/RT}}{\gamma(1 + 0.167\gamma) a_0^2 s_m N_t}$$
(36)

$$\Xi = \frac{\text{flux towards a clean surface}}{\text{rate of insertion in a cluster}} = \frac{\chi}{\sqrt{2\pi M_k R}} \frac{e^{(E_d - E)/RT}}{s_m a_0^2 \sqrt{T}} P_{\text{SiH}_4}$$
(37)

being $\gamma = \lambda / a_0$ the reduced edge spacing and χ a sticking coefficient. It can be observed that while ξ is an intrinsic parameter of the system, Ξ is instead a control parameter which accounts how the external variables as pressure, temperature, reactants concentration and gas velocity affect the surface processes. Actually, the role of temperature is twofold since it can affect also ξ through the ledge distance λ . It is interesting to explore the behavior of the system in a steady state growth (*i.e.*, $\partial N_k / \partial t = 0$) where k running from 1 to s_m .

The model above can be numerically solved by investigating the influence of the parameters ξ and Ξ on the surface coverage and clusters formation.

The results obtained for a surface temperature of 900°C and for some reasonable ξ values will be here summarized. In particular, two cases were considered. The former assumes $E_d = E_{in}$, while the latter assumes a difference between the two values of about 3 kcal/mol. The latter value is in the expected order of magnitude between the activation energy for the surface migration of an adatom and its insertion in a terrace kink. In the considered framework, the surface coverage is given by the ratio $\theta = N_i / N_t$, while the cluster coverage θ_c is given by the difference ($\theta_t - \theta$), being θ_t the total coverage calculated as follows:

$$\boldsymbol{\theta}_{\mathsf{f}} = (\mathsf{F} - \mathsf{F}_{\mathsf{s}})/\mathsf{F} \tag{38}$$

where F and F_s are the fluxes of SiH₄ toward the surface and the one of silicon atoms toward the steps, respectively. The balance of total adsorbed silicon atoms can be written as:

$$N = \sum_{s \ge 2}^{s_m} s N_s(\theta) = \sum_{s \ge 2}^{s_m} s \frac{k_1}{k_s} N_1(\theta) = N_t \theta \sum_{s \ge 2}^{s_m} s^{1-p}$$
(39)

and the mean s_m values that fits the previous equations yields an approximate value of the maximum cluster size. Examples of the calculations are reported in Fig. 13. They can be validated by the comparison with the experimental STM images of silicon surface reported in Fig. 14 [75,93,94] where the presence of clusters on the flat silicon surface is evidenced.



Fig. 13. Calculated surface coverage as a function of parameter Ξ (proportional to silane partial pressure) for two different increasing values of ξ .

Increasing ξ the surface coverage decrease together with the average number of atoms in the cluster (*e.g.*, from an average number of about 8 to an average to an average number of 2-3). The details of whether deposited material on a flat surface could form planar films or island with particular orientations, shape and size distribution are still matters of research and debate. In such a framework the mentioned with results reveal a high sensitivity to surface kinetics as a consequence of the energetic details of surface itself. This fact stresses the importance to investigate such aspects in order to be able to predict the epitaxial film homogeneity from operative conditions.



Fig. 14. STM images of Si surface [75,93,94]. (a) Individual atoms over a terrace. Rugged lines corresponds to surface step edge. (b) Formations of islands over the surface.

6. APPLICATIONS OF CVD

As already illustrated in Table 2, CVD is used to deposit layer of epitaxial semiconductor (such as Si or Ge), compound semiconductors (such as GaAs, AlGaAs or InP), insulators (such as SiO_2 or Si_3N_4) and conductors (such as W or Al). Considering this great amount of processes, many of them could be described more in detail to illustrate the concepts discussed above. We decided to focus our attention on deposition of epitaxial films and in particular the following important examples will be analyzed more in detail: the silicon deposition in barrel reactor and the InP and GaAs deposition in horizontal reactors. Regarding the latter example, the attention will be focused on the carbon incorporation issue.

6.1 Modeling of epitaxial silicon deposition in barrel reactors

Most of the industrial epitaxial silicon depositions are nowadays performed using barrel reactors due to their possibility to process a high number of wafers per batch. The wafers, usually ranging from 12 to 24, are held by a heated prismatic susceptor contained in a quartz bell externally cooled by air. Different commercial reactor configurations exist with main differences in the bell-jar shape and in the gas inlet apparatus (e.g., the Applied Material, the LPE or the Spire types). The barrel reactors operate at nearly atmospheric or at reduced pressure and with temperature ranging from about 500 K of the external wall to about 1500 K of the susceptor for the epitaxial silicon deposition case [95,96]. Such a high temperature gradient affects the system fluid dynamics that result in a mixed flow regime (e.g., natural + forced convection) [26,26,34,97]. Complex, buoyancy driven, secondary flows are then observed, and detrimental effects on film uniformity and interface abruptness arise [16]. Previous investigations demonstrated that, for the conditions above, the deposition is under mass transport control and it is strongly influenced by the thermal diffusion effects [34,42,97]. Accordingly, the performances of those reactors and, in particular the thickness uniformity of the deposited film, are heavily influenced by their fluid dynamics regime.

As a first approximation, the study of such reactors can be performed through simplified 1D models based upon the boundary layer theory [10,12,98]. Unfortunately, the level of optimization required by the microelectronics applications today cannot be met with the previous approach. Accordingly, the barrel reactor optimization and design can be performed only through models where the geometry and the reactor fluid dynamics are accounted in detail [34]. Furthermore the gas motion in the inlet zone has a strong influence on the deposition profile and such effect cannot be satisfactorily understood with simplified approaches [7,8].

Despite their industrial importance, only a few modeling attempts of barrel reactors were reported in the literature presenting different levels of approximation. The older 2D models always neglect to consider the inlet zone [11,99,100] or they consider a simplified inlet nozzle [9]. A 3D fluid dynamics in a 3D axial-symmetric system was more recently presented to consider the asymmetries of the gas inlet apparatus in a AMT type barrel reactor, where also the susceptor rotation was included but the geometrical representation of the reactor was still oversimplified [16]. The same approach was adopted, for a LPE type reactor, where a particular attention was placed upon the role of inlet apparatus and baffles insertion [13-15]. There, a 3D fluid dynamics in a 2D axial symmetric geometry was adopted due to the intrinsic symmetries of the examined reactor. All the modeling works above summarized were based upon the integration of eqs. (1) - (4), in the considered geometrical sketch of the reactor geometry. Since the geometric configuration of the simulations mostly relies on

the capability to solve the mentioned conservation equations in the specific geometrical situations.

As representing example of the above simulations, the epitaxial silicon deposition in two different commercial types of barrel reactor and two different deposition precursors will be here illustrated. In the former case, the silicon film is grown from SiCl₄ in a LPE 861 reactor [13-15], while in the latter the deposition occurs from SiHCl₃ in a AMT 7700 reactor [17]. In both cases the precursor is diluted in hydrogen, while all the operative conditions are summarized in the cited references. As already pointed out, in the high temperature deposition condition here examined (*e.g.*, T_{substrate} = 1200°C), the rate determining step of the overall process is the transport of the precursor from the bulk fluid phase to the substrate surface and consequently the fluid dynamics become of crucial importance for process description and control.

The role of the gas inlet apparatus in the LPE reactor is then illustrated in Fig. 15, where calculated streamline and temperature fields are reported for two different cases. A great cold-core laminar recirculation cell above the susceptor was observed for the case where the gas is fed through a shaped horizontal disk (run 2). That cell was generated not only by the combination of the buoyancy forces and of the susceptor rotation, but mainly by the radially directed inlet gas velocity. Significant differences can be evidenced in the other case where the gas inlet apparatus was omitted (run 1). There, the recirculation cell is counterotated and less marked than in the previous case. Furthermore, a second smaller recirculation cell is evidenced in correspondence of the inlet zone of the annular duct. The differences among the two simulations are even greater when the comparison between the calculated and the experimental deposition profile is considered as illustrated by Fig. 15(c). It can be observed that neglecting the gas inlet apparatus leads to an unrealistic estimation of the growth rate profile. On the contrary, the experimental growth rate profile can be satisfactorily predicted when the proper reactor geometry is considered for the simulations. Accordingly, the proper design of the gas inlet apparatus has a great influence on the reactor optimization with respect the increase of film thickness uniformity.

An idea of the system sensitivity to the process and to the geometrical parameters can be obtained by the inspection of Fig. 16, where the effects of alteration in the external bell diameter and in the carrier flow rate are illustrated. In these cases, the streamline and the temperature fields are not reported, because they are qualitatively similar to those of Fig. 15. In both the examined cases the simulations still show a good agreement with the experimental growth rate data without the use of adjustable parameters in the model.



Fig. 15. Calculated temperature field (left) and streamlines (right) without (a) and with (b) gas inlet apparatus; (c) comparison of calculated (—) and experimental (\blacksquare) growth rate data along the wafer midline for cases (a) and (b) [15].



Fig 16. (a) Role of bell diameter and (b) of carrier flow rate on growth rate uniformity along reactor longitudinal coordinate. Experimental data represented with points and calculated values with lines. [15].

The role played by the inlet apparatus is even greater if a different kind of barrel reactor is considered [17]. Two inlet flow rates can be evidenced in these reactors. The former, usually indicated as *main*, is introduced through the lateral jets, while the latter, indicated as *rotation* is introduced through the reactor ceiling, being its 25% injected as purge gas inside the susceptor, while the remaining 75% injected vertically along the bell wall and around the susceptor hanger. Usually, the deposition precursor is introduced diluted into the main flow rate. Because the precursor adopted in the

considered example (e.g., SiHCl₃) easily decomposes to the main specie responsible of film growth (e.g., SiCl₂), the following gas phase reaction have to be considered in the simulations: SiHCl₃ \leftrightarrow SiCl₂ + HCl [101,102]. Furthermore, in this example, to reduce the fully asymmetric 3D system to a axisymmetric 2D system, the gas inlet apparatus can be approximated to a circular corona injecting in each section the corresponding amount of flow rate, as it is sketched in Fig. 17. Moreover, being the jets flow directed towards a vertical deflector, a deflecting angle can be tuned during some test simulations on the experimental growth rate data. Then, the obtained value must be kept constant for all the remaining simulations.



Fig. 17. Sketch of the gas inlet apparatus approximation in the considered 2D geometry [17]

The comparison between the calculated and the experimental growth rate data measured in the longitudinal midline of the susceptor is illustrated in Fig. 18, while in Fig. 19 are illustrated the calculated streamlines, isotemperatures and SiHCl₃, SiCl₂ and HCl weight fraction within the reactor. It can be seen that the temperature field within the annular section of the reactor is quite regular. It is noteworthy that SiHCl₃ decomposed very soon inside the reactor and that HCl accumulates in the top part of the reactor (i.e., in contact with the reactor ceiling). The latter aspect is very important regarding corrosion problems and related contamination issues.

Using the inlet flow angle tuned to reproduce the experimental growth rate profile of Fig. 18 (i.e., $\beta = 80^{\circ}$), new simulations can be performed entering also the rotation flow rate. As illustrated in Fig. 20, the simulation indicated as *base* still well reproduces the experimental growth rate data. In the same figure, it is also illustrated the system sensitivity to the bell tilting increase (*i.e.*, from 0.6° to 1.5°) and to the rotation flow rate inlet distribution. Finally, the data reported in Fig. 21 show the alteration of the growth rate profile when a different flow rate distribution between main and rotation is adopted. The same figure shows also the sensitivity of the calculated results to the external wall temperature. Being the latter parameter out of control in the examined kind of reactors, the simulations show how its control could benefit the control of growth rate uniformity within the reactor.



Fig. 18. Comparison between calculated and experimental growth rates [17]



Fig. 20. Sensitivity of the growth rate profile as a function of altered flow rate and bell tilting with respect the base case [17]. O experimental data in condition of base case.



Fig. 19. Calculated streamlines, isotemperatures and main species weight fractions [17]



Fig. 21. Comparison between calculated and experimental growth rates (\bullet) for a different feed flow rates distribution. Sensitivity to wall temperature [17].

As illustrated in the above analyzed examples, one of the most important features of the CVD models based on a detailed fluid dynamics description is that they can be used to perform reliable sensitivity analysis. Thus, the parameters that affect to the greatest extent the physical and chemical behavior of the system can be identified. Moreover, they can be successfully applied to speed up the search of the optimal operating conditions that enables the production, at relatively high rate, of good quality materials.

In particular, if the modeling approach is systematically used at design stage as sketched in Fig. 22, dramatic cost savings can be safely predicted in developing new reactor configurations with respect the use of the standard *trial and error* procedure. Presently, the bottle neck of the illustrated procedure is the direct link of CAD software to the computational fluid dynamics codes used to solve the model equations, but this problem is expected to be solved soon.



Fig 22. Conceptual steps for CVD reactor design using detailed reactor models.

6.2 Modeling of epitaxial III-V semiconductors deposition in MOCVD reactors

An interesting example where the kinetics aspects are more relevant is the deposition of semiconductor compounds, conveniently deposited from gas phase using metal-organic precursors in open cold wall reactors. In fact, MOCVD processes require a moderate costly equipment and they are characterized by a higher productivity with respect to the use of Molecular Beam Epitaxy apparatus. Among the high number of III-V and II-VI interesting semiconductor compounds, the deposition of epitaxial InP on (100) surface using trimethylindium (TMIn) and phosphine will be investigated here with attention focused on the determination of a film growth mechanism based only on elementary chemical reactions.

Because the lack of experimental data for many reactions involved in the mechanism, their rate constant values have to be estimated by thermochemical methods [64,65]. The final result is to introduce in the model a high number of external parameters that in principle allow the fitting of any set of data. If the aim is to obtain a mechanism of general validity, such a procedure should be avoided and only a careful *a posteriori* validation of the estimated value must be done. For this reason, the model should be consistent with reported experimental trends for several different studies, rather than to exhibit an exact agreement with only one particular set of data. Accordingly, the mechanism validation could be performed by the comparison with

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experimental growth rate data measured by different authors in different operating conditions [73,103-105]. Being, all the above growth experiments performed in horizontal reactors, the 1D model previously discussed can be used for the simulations, being the attention mainly focused on the chemical mechanism testing that on fluid dynamics issues.

A detailed description of the gas phase mechanism involving TMIn, PH₃ and their fragments can be found in [73], but the main issues on the developing of a detailed chemical mechanism are centered on the description of the surface chemistry. The growing surface can be described by means of two different kinds of surface sites, where the gas species selectively adsorb. In particular, the gaseous species adsorb with a dual-site mechanism over a surface site corresponding to the opposite atom (*e.g.*, In on P and P on In) [55]. Hydrogen and methyl radicals can adsorb on both sites instead. The reaction considered in the mechanism have been already summarized in Table 3.

The first deposition process simulated here is the InP atmospheric growth on GaAs (100) substrates in cold wall reactor [73]. The comparisons between the calculated and the experimental data for two different sets of operating conditions are illustrated in Fig. 23 evidencing a good agreement between the reported data. At 490° C a sharp decay in the experimental growth rate can be observed due to the transition from the mass transfer to the kinetic controlled regime. The rate determining step in the latter case is the desorption of hydrogen from P sites (reaction S10 of Table 5). These result points towards the fact that at low substrate temperatures the growth of the film is inhibited by a surface reaction and not by a gas phase one, such as the TMIn or PH₃ decomposition.



Fig. 23. Comparison between experimental growth rate data (O)[73] and calculated values (---) [55].

To test the model predictions for low pressure working systems also the deposition in a commercial Aixtron 200 reactor operating at 20 mbar can be

considered [103]. In such a system, the InP substrate is placed in the middle of the susceptor. The model sensibility to feed precursor is illustrated in Fig. 24, where the inlet mole fraction of PH_3 is independently varied while the substrate temperature (640°C) and the partial pressures of the other components are kept constant. The growth rate diminishes when raising the PH_3 partial pressure. This is an expected behavior, since the adsorption process of PH_3 is always dual site, thus for every PH_3 molecule adsorbed, two surface sites disappear (reaction S5 and S6 of Table 5), inhibiting the interface reactivity and the film growth rate. This result strongly suggests that the dual site adsorption mechanism here proposed may be the correct way to understand the surface chemistry of InP films grown through MOCVD techniques.

An other interesting system to be simulated is still a low pressure reactor [104]. In this case, differently than the previous example, the outer wall is not externally cooled. The agreement between the calculated and the experimental growth rate data is satisfactorily depicted in Fig. 25. A decrease of growth rate value can be evidenced for temperatures greater than about 700°C. Also in the considered case, the model is able to depict the experimental trends in all the three evidenced growth regimes (*i.e.*, H₂ desorption at low temperatures, TMIn supply to the surface at intermediate temperatures and InCH₃ desorption at higher temperatures).





Fig. 25. Comparison between experimental growth rate data [104] (O) and calculated values (----) [55].

As a final point of the discussion section, it is important to remark that none of the model parameters was altered in simulating each one of the experimental trends above reported. These findings demonstrate the predictions of the proposed kinetic model and suggest its reliable application also outside the considered field of validation.

It could be worthwhile to devote more effort to the chemical mechanism of growth in the more usual deposition processes involving the mass transport controlled regime. This contrasts, it is important to note, with the more usual situation of the growth of semiconducting compounds where the issues of film composition are particularly important. This aspect can be better understood if our attention will be focused on the important aspect of the carbon incorporation inside the film when organometallic precursors are used. The latter aspect is particularly relevant when the growth of GaAs is examined.

The chemical mechanism of GaAs growth has been lengthy discussed in the literature [106-110]. In particular, the GaAs growth from trimethylgallium and arsine or trimethyl arsine will be considered. Here, only the main deposition pathways are sketched in Fig. 26, being the issues related to the developing of the mechanism similar to those already discussed for InP and specifically reported in the cited literature. The gas phase mechanism includes the unimolecular decomposition of the gallium precursor, while the reactions involving arsenic precursors are less important due to the high excess of arsenic precursors usually adopted in the examined growths. The surface mechanism includes chemisorption of trimethyl and monomethyl gallium, arsine and arsenic dimer. The desorption of monomethyl gallium is of particular importance for the growth rate decrease encountered at higher temperatures. Most of the above finding have been experimentally verified through surface science methods [111,112]. Particularly important to our points is the carbon incorporation mechanism through the formation of gallium carbene compounds. This aspect is particularly important from a technological point of view because it is now related to the possibility to obtain sharp doping transitions in heterojunctions bipolar transistors. Accordingly, the possibility to intentionally doping at high level by means of carbon incorporation is becoming an interesting feature as well as the almost total avoiding of non intentional carbon incorporation. The mechanism of carbon incorporation has been extensively discussed in the literature, being the carbene route the most credited mechanism [113-124].

Accordingly, introducing the overall GaAs growth mechanism and the carbon incorporation one in a monodimensional reactor model such as the one described in section 2, the deposition and the carbon content profile within the reactor can be obtained. The results of the simulations are illustrated in Fig. 27, where the amount of carbon incorporated in the film is plotted as a function of the deposition temperature. Different arsenic precursors (e.g., AsH_3 and $As(CH_3)_3$) are considered, as well as different V/III ratio.



Fig. 26. Sketch of the precursors decomposition pathways for gallium arsenide growth and related carbon incorporation within the film [113,114].



Fig. 27. Comparison between calculated and experimental values of carbon concentration in GaAS films as a function of deposition temperature and V/III ratio [113,114].

7. CONCLUDING REMARKS

The reported examples illustrate the status of modeling some of important aspects that are of interest in thin films growth by gas phase deposition. Obviously, many other aspects are of comparable interest, such as all the phenomena involved in the growth at feature scale, in particular when the trench filling is considered.

Also from the deposition reactor point of view, many other systems are of interest besides those here examined more in detail. Our attention was focused mainly on barrel reactors because their industrial importance and because there is still the need of more work to do for the optimization of the current generation and for the design of the next one.

About the developing of detailed chemical mechanism, the choice to examine Si, GaAs and InP among all the possible systems was done because our previous work in the field.

The reported examples stress also the shifting from the simulations at macroscale to those at microscale. This trend is directly connected to the film quality issues that represent the challenging question of the next future.

LIST of SYMBOLS

a ₀	crystal lattice constant
b	scaling factor
Ci	molar concentration of ith specie
C ^S _{im}	molar concentration of adsorbed <i>ith</i> specie on <i>mth</i> kind of surface site.
C _p	heat capacity
D	strength of the thermal noise
D	surface diffusion coefficient.
Di	effective diffusion coefficient of <i>ith</i> specie.
E _k	activation energy of kth reaction.
F	flux towards the growing surface.
F	overall mass flow rate.
g	gravity acceleration constant.
h(x)	surface coordinate.
ħ	mean value of surface coordinate.
h _s	heat transfer coefficient.
Н	reactor height.
H	surface energy.
k _B	Boltzmann's constant.
k _{ci}	mass transfer coefficient of ith specie.
k _k	rate constant of kth reaction.
k _T	thermal conductivity.
Ι	identity matrix.
L	linear size of a system.
M _i	molecular weight of <i>ith</i> specie.
M _s	molecular weight of the solid film.
Mw	average molecular weight of the mixture.
n	normal unity vector.
Ni	mass flux towards the deposition surface of <i>ith</i> specie.

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N _{1,2,}	surface concentration of adatoms and clusters.
P _{ik}	surface reaction order with respect ith component in kth reaction.
Р	system pressure.
Pi	partial pressure of ith gas specie.
q _{ik}	reaction order of <i>ith</i> specie in <i>kth</i> reaction.
R	gas constant.
Re	Reynolds number
$\widetilde{R}_{\mathbf{k}}$	rate of kth chemical reaction.
Sc	Schmidt number.
Se	external tube surface per unit reactor volume.
Sh	Sherwood number.
Sv	deposition surface per unit reactor volume.
t	time.
Т	temperature.
Т _G	gas temperature.
T _R	critical roughening temperature.
T_W	external wall temperature.
T _C	cooling fluid temperature.
TS	susceptor temperature.
Tm	melting temperature.
U	overall heat transfer coefficient.
v	gas velocity (vector).
V	reactor volume.
Z	reactor coordinate.

greek letters

α, β, z	scaling exponents.
α_{Ti}	thermodiffusion factor of <i>ith</i> specie.
γ	steric factor.
δ()	Dirac function.
$\Delta \tilde{G}_k, \Delta \tilde{G}_k^\circ$	Gibbs free energy changes.

 $\Delta \widetilde{H}_m, \Delta \widetilde{G}_m$ molar heat and free energy of melting.

 $\Delta \tilde{H}_k$ enthalpy change of *kth* chemical reaction.

- $\eta(\mathbf{x},t)$ thermal noise.
- λ terrace width.
- Λ cutting parameter.
- μ gas viscosity.

ν	specific surface energy.
ν _{ik}	stoichiometric coefficient of <i>ith</i> specie in <i>kth</i> reaction.
θ_{v}	fraction of free surface sites.
ρ	gas mass density.
ρ_s	mass density of solid film.
σ(L)	interface roughness.
φ ₀	specific reticular potential energy.
Ψ	overall surface concentration of surface sites.
$\Psi_{\rm m}$	overall surface concentration of mth kind of surface site.
χ	self affine coefficient.
ω	mass fraction of <i>ith</i> specie.
Ω	reactor free cross section.

supercripts

G	gas
S	surface
Т	transposed vector
0	inlet or boundary conditions

subscripts

i	specie index
k	reaction index

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