

A MULTISCALE APPROACH TO THE STUDY OF EPITAXIAL FILM EVOLUTION DURING MOCVD

Alessandro Veneroni¹⁾, Carlo Cavallotti¹⁾, Maurizio Masi¹⁾, Davide Moscatelli¹⁾, Sergio Carrà¹⁾

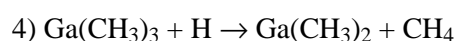
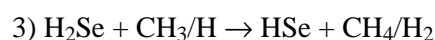
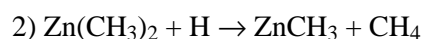
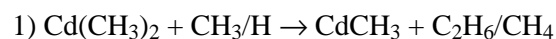
¹⁾ Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, via Mancinelli 7, 20131, Milano, Italy

The Metal Organic Chemical Vapor Deposition (MOCVD) of GaAs, GaN, ZnSe, CdTe and AlAs is widely used for the manufacturing of electronic and optoelectronic devices. The growth is usually determined by the interaction of gas phase precursors with a heated substrate. The quality of the grown film, which depends greatly from the operating conditions of the deposition reactor, is a key parameter in the optimization of the MOCVD process. For this reason it is extremely important to have a good comprehension of the chemical and physical phenomena that take place during the film growth and in particular of the gas phase and surface chemistry of the deposition process [1].

In this work we present a multiscale approach meant to describe the film evolution at different time and length scales. The gas phase and surface chemistry active during the growth of CdTe, ZnSe, GaAs and GaN were investigated with quantum chemistry. Then we studied the reactor fluid dynamics and overall mass and temperature balances with the finite element method. Finally, the morphological evolution of the film is investigated with 3D kinetic Monte Carlo.

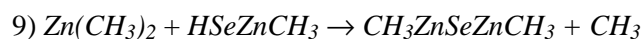
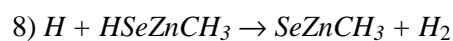
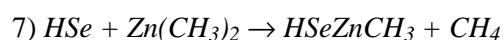
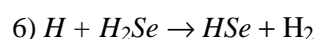
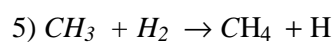
Quantum chemistry calculations were performed with density functional theory. The Becke 3 parameters and Lee Yang Parr functionals were used to evaluate the exchange and correlation energy. Among the different basis sets considered the best agreement with calculated experimental bond energies was obtained with the all electron 6–311 basis set with added polarization and diffusion functions (6–311G(d,p)). However similar results were produced with a much smaller basis set adopting the Dunning/Huzinaga valence double zeta basis set on the first row atoms and the Stuttgart/Dresden effective core potential basis set on the others (briefly, SDD). Therefore the following strategy was adopted in the calculations: first structures and energies were determined with the SDD basis set, then geometries so optimized were used as input for calculations with the larger basis set.

The main results of the quantum chemistry calculations performed on gas phase reactions is that radical reactions between CH₃ and in particular H radicals and gas phase metal organic molecules such as Cd(CH₃)₂, Zn(CH₃)₂, H₂Se, and Ga(CH₃)₃ are fast and can contribute significantly to the decomposition of the metal organic molecules, and thus they can greatly enhance the gas phase reactivity. In fact, CH₃ is produced at a high rate during a MOCVD growth process as a result of the dissociative adsorption of the metal organic precursor on the growth surface, which is usually followed by the desorption of the organic fragments [1,2]. If H₂ is used as carrier gas, atomic hydrogen can be easily produced by reaction between CH₃ and H₂. Among the investigated gas phase reactions are:



Activation energies calculated at the B3LYP level for reactions 1–3 are 16800./6300, 17450, and 4000/0. kcal/mol, respectively. As it can be observed, reactions with hydrogen have much lower activation energy than those with CH₃. Since the film growth rate is directly related with the reactivity of the gas phase, this result (i.e. the high

reactivity of MO molecules with H) might explain the increase of growth rate often observed when performing the deposition process in a H_2 atmosphere with respect to a He atmosphere. The radical mechanism here proposed can also account for the formation of the large gas phase adducts often observed during the MOCVD of ZnSe, which are known to be detrimental for the film quality [3]. In fact, the formation of MO radicals in the gas phase can start a radical chain process characterized by the successive addition of Zn and Se units. In particular, for a gas phase containing H_2Se and $Zn(CH_3)_2$, we found that the following reaction chain mechanism, which results in the formation of the adduct $CH_3ZnSeZnCH_3$, is very fast and proceeds through a succession of almost barrierless reactions:



The calculated transition state for reaction 9 is reported in fig. 1.

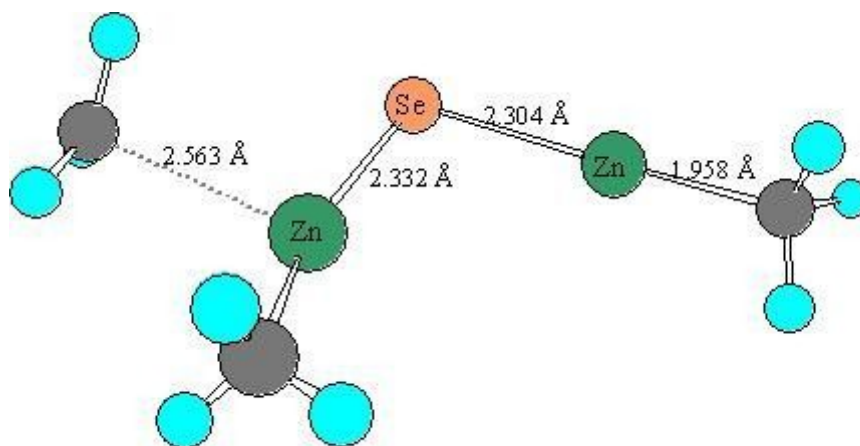


Fig. 1. Transition state calculated at the B3LYP/6–311g(d,p) level for the reaction between $Zn(CH_3)_2$ and CH_3ZnSe to form the adduct $CH_3ZnSeZnCH_3$.

The reaction of $Ga(CH_3)_3$ with H follows a different pathway, characterized by the addition of H and the loss of a CH_3 group to give $GaH(CH_3)_2$, which can then react fast with CH_3 resulting into $Ga(CH_3)_2$ and CH_4 . Similarly, $Ga(CH_3)_3$ reacts fast (the reaction is barrierless) with NH_2 , which can be easily generated during the GaN MOCVD, to give $Ga(CH_3)_2NH_2$. This molecule is known to be an important intermediate for the growth of GaN and this mechanism is likely to be faster than the addition–reaction mechanism usually proposed. This result is in agreement with recent experiments and calculations, which show that the GaN gas phase reactivity might be more complicated than assumed until now.

The approach used to study the surface reactivity is similar to that adopted for the gas phase. Accordingly, experimental kinetic constants were used whenever available and were calculated through density functional theory in the other cases. Kinetic constants of unknown surface reactions were investigated with a cluster approach. Clusters of different dimensions and structures were considered and the most valid were identified

through comparison with experimental data. In general, there are two problems associated with the simulation of a surface through a cluster: the errors in reproduction of long range effects and underestimation of the hindrance effects due to the presence of neighboring atoms not explicitly considered. The first problem is lesser important for semiconductors such as those here considered than for metals due to the covalent nature of the bonds. In order to increase the stability of the cluster and avoid the presence of unpaired electrons, hydrogen atoms were added consistently with the electron counting rule. The second problem was resolved by increasing the dimension of the cluster. The structure of the cluster used to study the surface reactivity of AlAs and GaAs is reported in fig. 2.

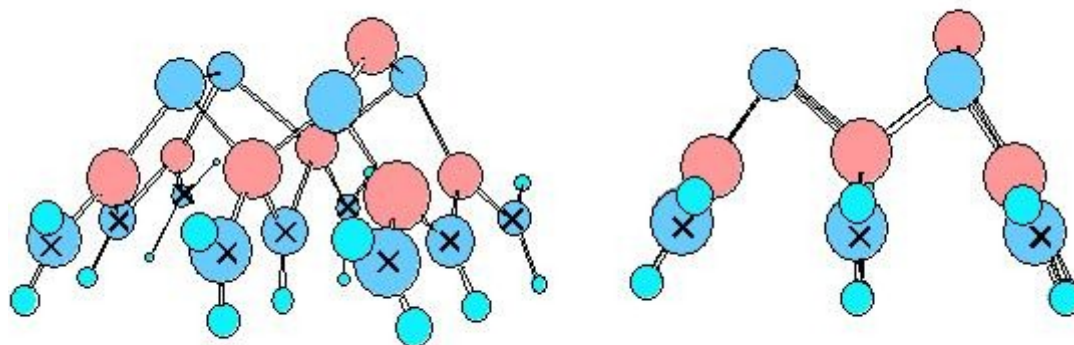


Fig. 2 Structure of the cluster used to simulate a β 2(2x4) As terminated surface (21–23 heavy atoms). Atoms that were held fixed in their lattice positions are marked with a x.

Energies for the adsorption of relevant metal organic molecules are reported in table 1.

Energy of adsorption (kcal/mol) of GaCl and GaCH₃ on the cluster of fig. 2. Structures and energies were computed at the B3LYP level with an effective core potential basis set.

Reaction	ΔH	ΔH	ΔH
	B3LYP/SDD	B3LYP/6–311+g(d,p)	(exp.)
As terminated surface – GaAs lattice			
GaCl* \rightarrow GaCl + sAs	26.4	34.2	38
Ga* \rightarrow Ga + sAs	47.3	63.4	n.a.
GaCH ₃ * \rightarrow GaCH ₃ + sAs	44.5	51.8	n.a.
GaCH ₃ * \rightarrow Ga* + CH ₃	54.6	46.9	46
AsH* \rightarrow H + sAs	44.5	50.8	n.a.

The local gas phase and surface composition active during the MOCVD of AlGaAs was studied inserting the developed kinetic schemes into a finite element model of the growth reactor. Results of the simulations are reported in fig. 3.

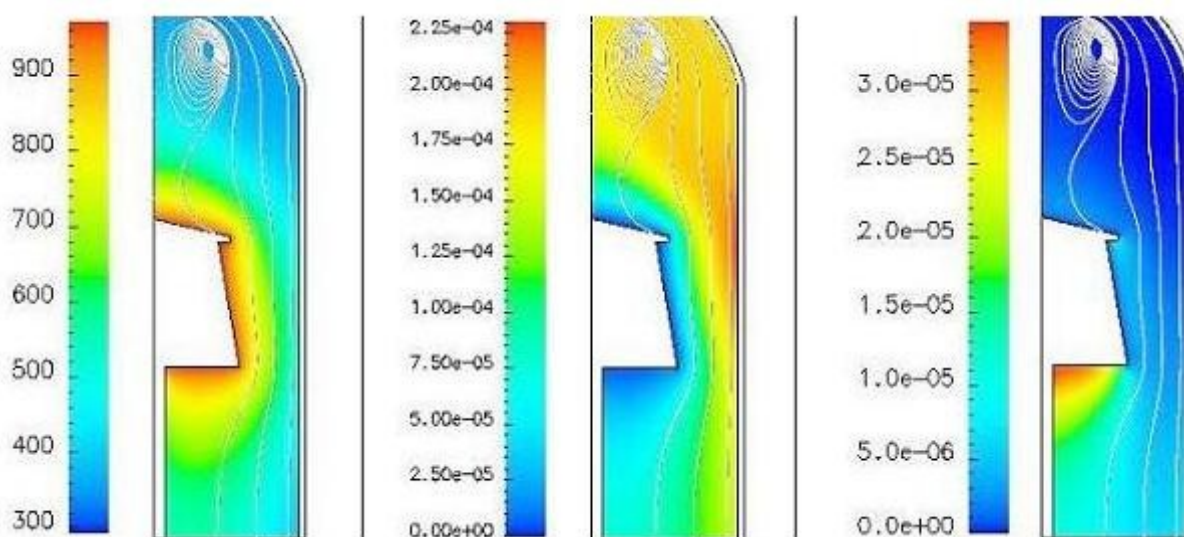


Fig. 3. Geometries of the reactors used in the simulations. Temperature fields and streamlines on the left. On the center and on the right are the $\text{Ga}(\text{CH}_3)_3$ and GaCH_3 calculated gas phase mole fractions.

Finally the morphological evolution and island density concentration were investigated with 3D kinetic Monte Carlo. The comparison between calculated and experimental island density is reported in fig. 4.

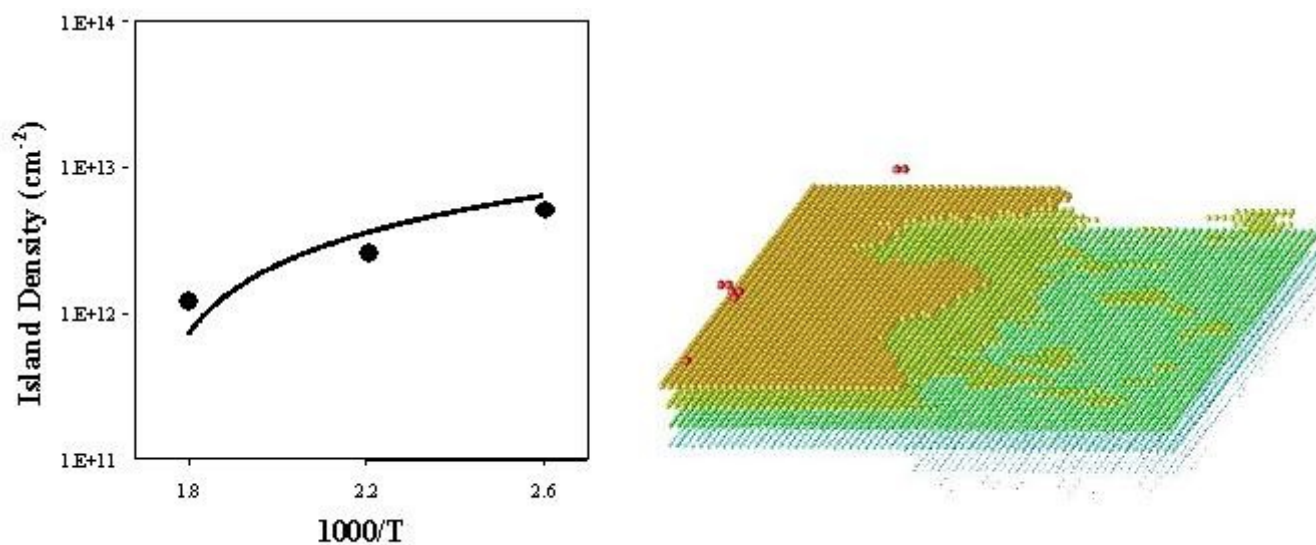


Fig. 4 Left: comparison between calculated and measured island density as a function of substrate temperature. Right: computed surface structure at low temperature.

References

1. M.L. Hitchman and K.F. Jensen, 'Chemical Vapor Deposition', Academic Press, London, 1993.
2. C. Cavallotti, V. Bertani, M. Masi and S. Carrà, J. Electrochem. Soc. 146, 3277 (1999).
3. D. Moscatelli, C. Cavallotti, M. Masi and S. Carrà, J. Crystal Growth 248, 31 (2003).