4. Monte Carlo and Kinetic Monte Carlo Methods

MC methods are stochastic. Through random sampling from certain probability distribution functions, which for example describe the velocity distribution of the atoms in an ideal gas, MC methods are used to solve partial differential equations (PDEs), which are very difficult to be solved deterministically, i.e. with classical numerical techniques for PDEs. The latter would require billions of degrees of freedom to describe the system or years of computational time for studying the evolution of the system or - in the worst-case scenario - both.

The basic MC method proposed in 1946 by Ulam et al. (1), initially for computing complex integrals via a stochastic way. It gain rapidly interest for solving general scientific and engineering problems especially after Metropolis et al. (2) who improved the method by introducing *importance sampling*. Importance sampling does not affect the computation of the integral *per ce* - compared to the original work by Ulam et al. - but provides a more sophisticated way for computing properties that depend of the complex interval, thus making MC method less time consuming and more efficient. Metropolis MC solves the Master Equation in equilibrium which, in its general form, reads,

$$\frac{\partial p_j(t)}{\partial t} = \sum_{i \neq j} p_i(t) T_{ij} - \sum_{i \neq j} p_j(t) T_{ji} \tag{39}$$

where p_j is the probability of the system to be found in state j at time t, p_i is the probability of the system to be found in state i at time t and T_{ij} and T_{ji} denote the transition rate or transition probabilities from state i to j and j to i respectively, such that, if the system is in state i the probability that the system jumps to state j during the subsequent time interval dt is $T_{ij} dt$. In general, $T_{ij(ji)}$ depends on the history of the system, but here we consider only *homogeneous Markov processes*, i.e. $T_{ij(ji)}$ does not depend on time and the systems current state depends only on its previous one and not on more previous states.

In equilibrium, and after some minor algebraic manipulations, Eq. (39) reads,

$$p_i T_{ij} = p_j T_{ji} \tag{40}$$

where the argument (t) is dropped since p_i and p_j in equilibrium are independent of time. Eq. (40) is termed as *detailed balanced* condition. The probabilities $p_{i(j)}$ in equilibrium obey a Boltzmann distribution,

$$p_{i(j)} = \exp\left(-\frac{E_{i(j)}}{k_b T}\right) \tag{41}$$

where $E_{i(j)}$ is the energy of the system in state $i(j)$.

The key point of Metropolis MC is how to choose T_{ij} without the detailed balance condition, Eq. (40), be violated. Eq. (40) can be re-written by considering Eq. (40) as,

$$\frac{T_{ij}}{T_{ji}} = \frac{p_j}{p_i} = \exp\left(-\frac{\Delta E}{k_b T}\right) \tag{42}$$

where $\Delta E = E_j - E_i$. Metropolis et al. proposed that,

$$T_{ij} = \begin{cases} 1, & \text{if } \Delta E \leq 0 \\ \exp\left(-\dfrac{\Delta E}{k_b T}\right), & \text{if } \Delta E > 0 \end{cases} \tag{43}$$

so that the system *will certainly move* from state i to j since *ΔE <0* but *the system may move* from state i to j with a probability $\exp\left(-\dfrac{\Delta E}{k_b T}\right)$ since *ΔE>0*. To sample from the distribution and move the system from state i to j in the latter case, a random number, ξ is chosen between (0,1] and if $\xi < \exp\left(-\Delta E / k_b T\right)$ the system moves to the state j, otherwise the move is rejected. Following Metropolis MC, different states of the system can be generated in a consistent way with a desired probability (rather than uniformly) and the thermodynamic average of a given quantity q_i can be computed from,

$$\langle q \rangle = \frac{\sum_i q_i p_i}{\sum_i p_i} \tag{44}$$

Kinetic MC (KMC) is a variant of MC method that solves the Master Equation, Eq. (39), but - in contrast to MC - not in equilibrium. Particularly, Bortz et al. (3) introduced the *N-fold* method. The *N-fold* method chooses and implements random configurational transitions with unit probability (i.e. unconditionally), and the choices are biased according to each transition's likelihood (i.e. transition rates) so that more likely transitions are chosen more often. The transition rates are often represented as the product of an attempt rate and the probability of success per attempt, which are formulated as exponential functions involving the energy barrier of the process. Every event i is assigned a rate r_i,

$$r_i = v_i \exp\left(-\frac{E_i}{k_b T}\right) \tag{45}$$

where v_i is a frequency prefactor, typically of the order of a vibrational frequency (10^{-13} s^{-1}) for surface processes and E_i is the energy barrier for the process and T is the absolute temperature. A KMC simulation proceeds by calculating all the rates r_i of the possible processes and then advancing the system by a single configuration change. In the *N-fold* method, the total rate, $R = \sum_i r_i$, is first computed and then a process n is randomly chosen according to,

$$\sum_{i=1}^{n} \frac{r_i}{R} < \xi < \sum_{i=1}^{n+1} \frac{r_i}{R} \tag{46}$$

where ξ_1 is randomly chosen in (0,1). The time is advance according to $t = t + \Delta t$. The time step, Δt, of the method is given by,

$$\Delta t = -\frac{\ln \xi_2}{R} \tag{47}$$

where ξ_2 is an additional random number chosen in (0,1).

4.1 The kinetic Monte Carlo method through a growth example

Here we present the *N-fold* method (3) as adopted for CVD and growth processes in general. We present the method assuming a simple cubic lattice for the crystal. We consider only the first-nearest neighbor interactions (4) which for the simple cubic lattice are maximum 5 as in Fig.14. For the shake of simplicity, but without loss of generality, we assume three events (or micro-processes) in the model: adsorption, surface diffusion, and desorption. We adopt the *solid-on-solid* approximation i.e. we do not allow overhangs during the growth of the film. The computational domain is a 2D lattice and the computations are pseudo-3D i.e. the
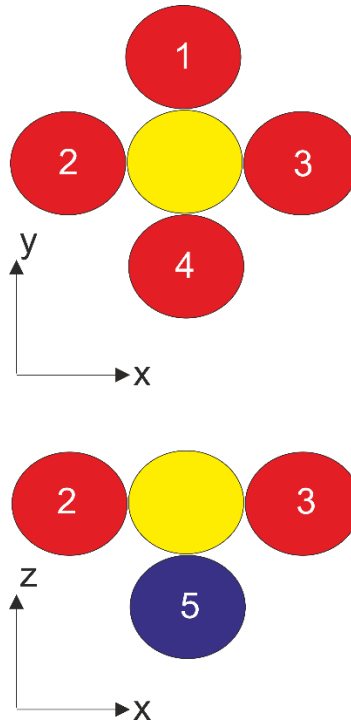

Figure 14: The 5 first neighbors in a simple cubic lattice. The yellow particle is a particle absorbed on the surface lattice. The red circles are sites in the lattice that particles can be absorbed in the same level as the yellow particle. The blue particle is a level below. The numbering is random. The maximum number of neighbors is 5 (all positions occupied by particles) and the minimum is 1 (only one particle in the low level – the blue circle).

third dimension is the height of the film during growth. The events are Markov processes (5, 6) with a transition probability per unit time.

The adsorption probability is the probability of a particle to stick on the surface of the wafer upon collision. Assuming ideal gases and based on the kinetic theory, this probability per unit time equals (7),

$$R_a = \frac{S_0 P}{C_{tot}\sqrt{2\pi m k_B T}} \tag{48}$$

where S_0 the sticking coefficient, P the partial pressure of the gas, C_{tot} the open cites in the surface, m the particles mass, k_b the Boltzmann constant, and T the temperature of the wafer.

The desorption probability depends on the local activation energy and the number of first-nearest neighbors and equals to,

$$R_d(n) = v_0 \exp\left(-\frac{nE}{k_B T}\right), \quad n = 1, 2, 3, 4, 5 \tag{49}$$

where E is the bond energy, v_0 is the desorption rate when $E = 0$ και n the number of the first-nearest neighbors that are connected to this particle.

The surface diffusion probability equals to,

$$R_m(n) = -v_0 \exp\left(\frac{E - E_m}{k_B T}\right)\exp\left(-\frac{nE}{k_B T}\right), \quad n = 1, 2, 3, 4, 5 \tag{50}$$

where v_0 is the diffusion rate when $E = E_m = 0$. E_m is the energy barrier for the surface diffusion of a particle to its neighbor position in a flat surface.

As in the conventional KMC method the time step is given by Eq. (47) with R, i.e. , the total rate of all process,

$$R = R_a N_T + v_0 \left[1 + \exp\left(\frac{E - E_m}{k_B T}\right)\right]\sum_{n=1}^{5} N_n \exp\left(-\frac{nE}{k_B T}\right) \tag{51}$$

where N_T is the number of the particles in the active surface and N_n the number of particles with n first-neighbors.

At $t = 0$ s the surface can be flat or have steps and must be updated after a process of adsorption, desorption or surface diffusion. This update is performed locally – only around the first-nearest neighbors – to avoid the high computational cost.

<mark>Periodic boundaries</mark> are imposed in the domain i.e. if a particle leaves the computational domain from one side of the lattice it returns to the computational domain
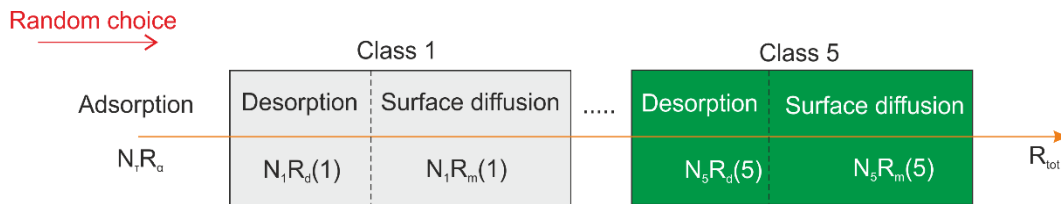

Figure 15: Selecting an event from a class. N_T is the total number of active sites (e.g. in a 10x10 lattice, $N_T = 100$), N_1 is the number of particles with one first-nearest neighbor etc.

from the opposite side. <mark>The absorbed particles are grouped together in classes according to the number of their first-nearest neighbo</mark>rs. All probabilities are computed *a priori* and every attempt is successful. Time increases according to the duration of each event (see Eq. 47). The algorithm starts by selecting a random number. According to its value, an event from a class is chosen and then randomly a particle from this class is chosen to perform this event. After each event the classes are updated and the probabilities are re-computed.
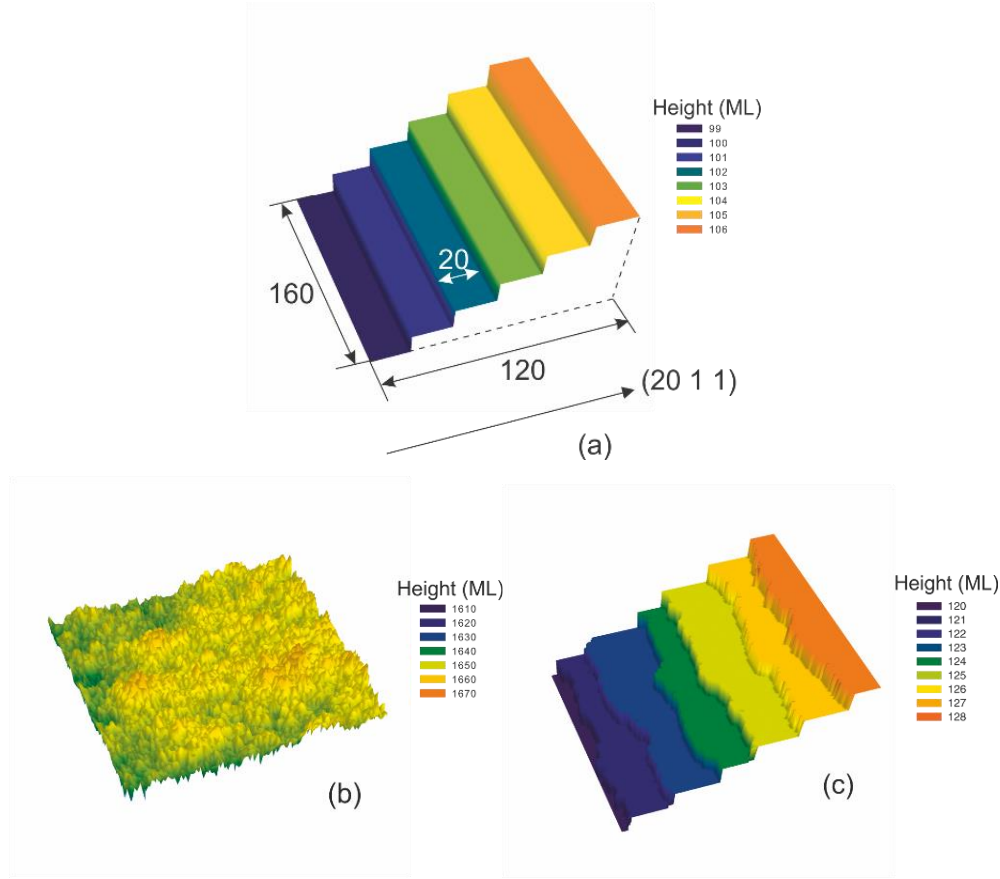
Figure 16: (a) Initial surface, t = 0 s, (β) nucleation, T = 500 K, t = 0.05 s and (c) step growth, T = 1100 K, t = 0.05 s.

Assuming the input parameters in Table 1 (7), and an initial stepped surface (20 1 1), the one in Fig. 16a, KMC computations are performed for two different wafer temperatures, namely T = 550 K and T = 1100 K. The results are shown in Figs. 17b-c. In Fig. 17b for T = 550 K, the initial steps have been destroyed because the rate of adsorption is higher than the rate of desorption. The final surface is characterized by high roughness. This type of growth is termed as *nucleation*. For T = 1100 K, the adsorption and desorption rates are almost equal. Thus, the initial steps are preserved in the final structure (see Fig. 16c). This type of growth is termed as *step growth.*

In Fig. 17 we compute the growth rate, the roughness and the class coverage, i.e. the number of particles belonging to a class normalized with the total number of surface sites, for different wafer temperatures. The growth rate is computed via the event counting method which

defines growth rate as the rate of adsorption divided by the rate of desorption. The roughness is computed according to (8),

$$\text{Roughness}: 1 + \frac{\sum_{i,j=1}^{N_s} \left(\left| h_{i+1,j} - h_{i,j} \right| + \left| h_{i-1,j} - h_{i,j} \right| + \left| h_{i,j+1} - h_{i,j} \right| + \left| h_{i,j-1} - h_{i,j} \right| \right)}{2 \cdot N_T} \tag{52}$$

where N_T is the size of the lattice (here 160x120) and $h_{i,j}$ is the height (thickness) of the film in the discretized cell i,j of the lattice.

Table 1 Input parameters for the KMC example.

S_0	P	M_r	C_{tot}	v_0	E	y	Lattice
[-]	[Pa]	[kg mol^{-1}]	[site m^{-2}]	[s^{-1}]	[kcal mol^{-1}]	[-]	
0.1	101325	$32 \cdot 10^{-3}$	10^{19}	10^{13}	17	$2 \cdot 10^{-4}$	160x120

As it is evidenced from Fig. 17, for the low temperatures the growth rate is high (more adsorption than desorption events) and as the temperature increases the growth rate decreases (adsorption events become equal to desorption events). As we can see the roughness follows the same trend as the growth rate; more adsorption events destroy initial smooth steps. Concerning class coverage, in low temperatures the particles are shared between the classes which explains the high roughness. On the contrary, in high temperatures almost all particles have all first-neighbors sites occupied, since $\langle \theta_5 \rangle$ approaches unity, resulting to a smooth film with small roughness. These results are in excellent agreement with the ones reported in (7).
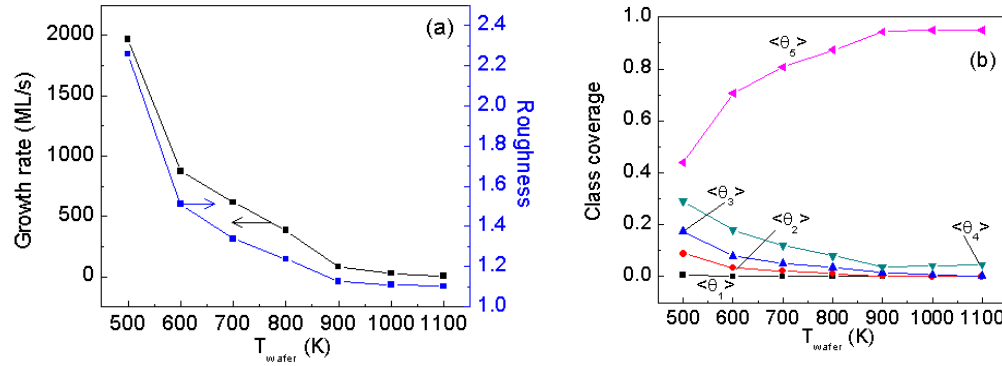
Figure 17: (a) Growth rate in monolayer per seconds (ML/s) and roughness.
(b) Class coverage for different wafer temperatures.

Through this simple example, the basic principles for modeling growth phenomena via the KMC method is presented. However, many detailed KMC models have been developed through the years for tackling problems from CVD processes and surface reactions in general. We recall the early work of Dufour et al. (9) concerning surface reactions in general, the work of Zieri et al. (10) in laser assisted CVD, the work of Kang and Weinberg (11) for surface reaction processes, the works of Battaille et al. (12, 13) for the detailed KMC model for the CVD of diamond and later in 1999 the work of Grujicic and Lai (14) for the CVD of diamond in a (111) oriented film, the work of Drotar et al. (15) where they explore how the re-emission mechanism affects the roughness of the growing film and the work of Kajikawa (16) again on roughness development of the film during CVD. We recall the work of Lartz et al. (17) who presented a self-learning KMC i.e. a KMC model where an *a priori* list of events is not needed but they are computed "on the fly". Tsalikis et al. (18) presented a model for the silicon (Si) deposition which includes 5 species and 29 reactions in Plasma-Enhanced CVD (PECVD) while Gunther and Fabian studied the CVD of silicon (Si) from 130 reactions. Bouhadiche et al. (19) presented a KMC model for the Si CVD from silicon nitride ($SiNO_x$). Rodgers et al. (20) proposed a 3D KMC model for the diamond growth and recently, Balbuena and Martin-Bragado (21) for the detailed study of Si CVD from SiH_4.

Excellent reviews on KMC methods for growth processes can be found in the early work of Gilmer et al. (22), the work of Chatterjee and Vlachos (23), the work of Voter (2007) (24) and

in the work of Battalie (25). For an introductory text for the KMC the interested reader is referred to Jansen (26).

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