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A novel kinetic Monte Carlo method for epitaxial growth[♣]

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A fast and realistic kinetic Monte Carlo method, aimed to reproduce pattern formation mechanism in epitaxial growth is presented. By several simple examples the applicability of the method is illustrated: dynamics and statistics of island growth and coalescence, impurity segregation and stacking fault dynamics. The method offers new perspectives for simulating hetero-epitaxial growth and the formation of several deposited layers in reasonable computational time, using normal PC type computers.

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1. Introduction

Kinetic (or resident time, or BKL-type) Monte Carlo methods are appropriate for simulating those dynamical phenomena where several processes with widely different time-scales are simultaneously present. In the case of epitaxial thin-film growth this is the case since: (i) atoms can be deposited on a crystalline surface with a given rate, (ii) atoms can diffuse on the surface (this diffusion being governed by different rates depending on the binding energy of the specific atom) and (iii) decohesion of adatoms from the surface are also possible (Fig. 1). In case of co-deposition of different type of atoms neighbouring atoms of different kind can exchange their positions (Fig. 1) following complicated microscopic mechanisms. This exchange is also characterized by a specific rate.

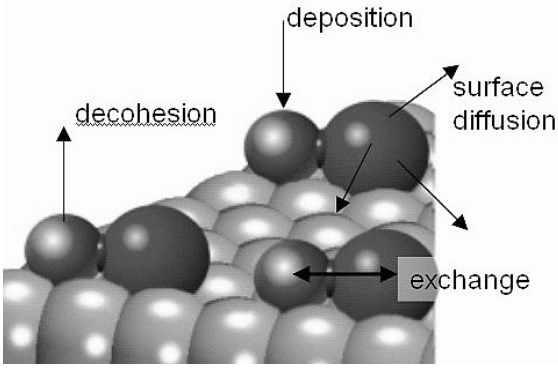

Fig. 1 Microscopic processes responsible for the dynamics of atoms during epitaxial growth.

For simulating the result of these microscopic processes with widely different rates, a Monte Carlo method used for studying equilibrium properties of low temperature systems (the BKL Monte Carlo method [1]) was adapted and named as kinetic Monte Carlo method (for a review see [2]). The main idea is that in each simulation step one process is probabilistically selected (with probability proportional with its rate) and carried out. The time is updated non-uniformly, depending on the rates of all possible processes at that given moment.

Generally, the **deposition rate** is fixed and calculated from the deposition speed (deposition flux) given as the number of new monolayers deposited in unit time (ML/s). The **diffusion rate** ($r_{X\to Y}$) of an atom is governed by the thermodynamic temperature (T) of the system and the potential barrier ($\Delta E_{X\to Y}$) that the atom has to overcome between the initial (X) and the final (Y) position:

$$r_{X\to Y} = f_0 \exp(-\frac{\Delta E_{X\to Y}}{kT}) \tag{1}$$

In expression (1) k is the Boltzmann factor and f_0 is the attempt rate, which is roughly the vibration frequency of atoms in the crystal ($f_0 \approx 10^{12}$ Hz). Since the value of the barrier is not straightforward to estimate (even if the pair-potential between the atoms is known), several simplifying methods are used [3]. The simplest approach is to consider the potential barrier dependent only on the binding energy of the atom in the initial X state [4-7] or by applying the transition state theory [8]. A better, but computationally more costly approach is to consider a realistic pair-potential between the atoms [9] and estimate the potential in several points between the initial and final state.

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The embedded-atom method [10,11] offers another possibility for estimating the potential barrier in the hopping process. In such case the difference between the maximum and initial value will yield the potential barrier. Nowadays, with the advances in ab-initio methods, DFT calculations can be also successfully applied to estimate the value of the potential barrier [3,12,13].

The **decohesion rate** is obtained either by fixing a phenomenological potential barrier E_{dec} for this process or by calculating the more realistic potential barrier from first principles, as the binding energy of the chosen atom at the given site.

Exchange between neighbouring and different type of atoms are microscopically realized through complex vacancy mechanisms. In KMC simulations however usually an oversimplified geometry is considered where many degrees of freedom for diffusion are not taken into account, so exchange possibilities are mostly blocked. The **exchange rate** is then usually postulated in form (1) by assigning a hypothetical E_{ex} potential barrier for this process.

Simulations are usually performed in a two-dimensional geometry [4-7], the atoms being allowed to occupy the sites of a pre-defined lattice. By this approach one reproduces an idealized situation where a new layer is growing on a perfect crystalline substrate. The simplest possibility is to consider square lattice and the sites on the growing layer positioned exactly on the top of the atoms forming the substrate [4-7]. In such manner sometimes non-realistic three-dimensional cubic structures are simulated. However, approaches on more complex geometries are also possible. One can use lattices with different symmetries and different stacking sequences for positioning the atoms in the growing layer [2,3,12]. Simulations can be made more realistic by considering a second layer on the top of the simulated one so that interchanges between these two layers become possible. This allows the formation of additional defects and vacancies.

Nowadays computationally costly off-lattice kinetic Monte Carlo methods [14,15] are also considered for the case when several types of atoms are simultaneously present and there is lattice constant or symmetry mismatch between the crystalline structures of the components. In such an approach the position of the atoms are computed from an energy minimization procedure and the dynamics of the system is realized with the kinetic Monte Carlo algorithm. The method is an optimal reconciliation between the realistic nature of the Molecular Dynamics simulations and the higher speed of the kinetic Monte Carlo approach. Although there are some interesting results obtained with this approach the method is still not usable for reasonably large system sizes and practically relevant evolution times in (2+1)D.

2. The MC method implemented in the present study

The kinetic Monte Carlo method implemented by us has a small number of undetermined phenomenological parameters and several additional degrees of freedom for the diffusion of the atoms. In the mean-time, the speed of the algorithm remains practically the same as in the case of the generally used classical methods.

Triangular lattice ((111) plane of fcc structure) is used as substrate (filled circles in Fig. 2). This leads to a more compact packing of the atoms than in the case of the square lattice. It is assumed that atoms are spheres. In such manner, there are two triangular sub-lattices (empty circles and crosses in fig. 2) on which the adatoms can be deposited, forming monolayer lattices of fcc or hcp crystalline phases. Due to geometric restrictions atoms in the growing layer cannot occupy neighbouring sites belonging to different sub-lattices.

Considering a bulk fcc substrate, stacking fault develops at the interface of the substrate and a growing hcp monolayer island (Fig. 3). By this manner phase boundaries will also appear between growing islands of fcc and hcp types. This extra defect mechanism characteristic for this geometry facilitates the diffusion and interchange of atoms. Diffusion of adatoms on the top of the first growing monolayer is also considered. These adatoms can also jump down on the substrate.

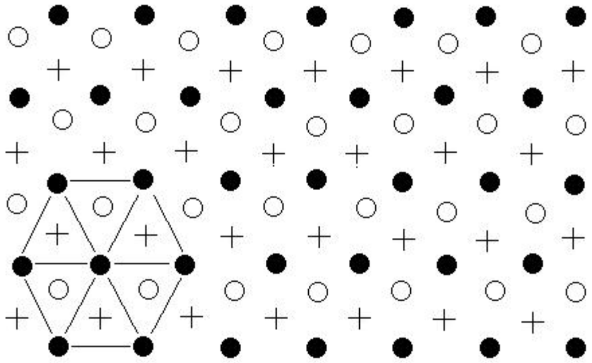

Fig. 2 Geometry of the considered lattice. Filled circles represents the sites of the substrate, empty circles and crosses represents the fcc and hcp lattice sites, respectively, on which the new layer can growth

For computing the potential-barrier that governs the surface diffusion of the atoms phenomenological pair-potentials are used. The hopping barrier for the diffusion process is calculated from the binding energies of the atoms in the initial and final states. As a first trial Lenard–Jones type pair-potentials were considered, although other accepted forms would probably lead to qualitatively similar results.

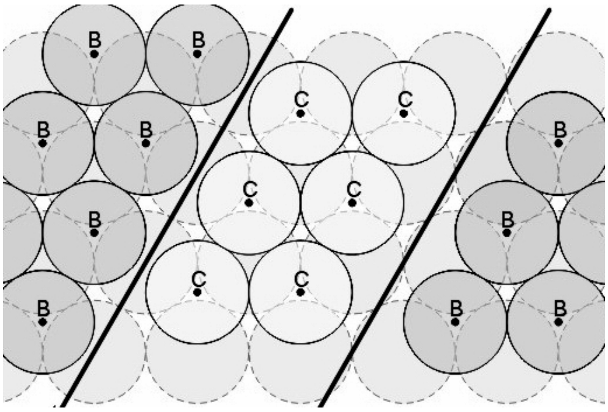

Fig. 3.Phase-boundaries that can be formed on the triangular fcc surface.

Assuming the lattice constant as length unit and Lenard-Jones type pair-potentials, the interaction potential between atoms of type W and Q separated with distance r can be written with one E_{WQ} parameter:

$$U_{WQ} = E_{WQ}\left(\frac{1}{r^{12}} - \frac{2}{r^{6}}\right) \qquad (3)$$

The parameter E_{WQ} determines the binding energy at the $r=1$ equilibrium distance. Interaction between atoms are taken into account up to $s=3$ lattice site distances. It is assumed that the hopping barrier from a site X to a site Y depends not only on the binding energy at site X, but also on the change in the binding energy. The following simple linear form for calculating the hopping barrier of an atom has been proposed by us previously [16]:

$$\Delta E_{X\to Y} = -\alpha E_n^X + (1-\alpha)(E_n^Y - E_n^X) \qquad (4)$$

In equation (4) E_n^X (E_n^Y) is the total interaction energy (binding energy) of the atom at sites X (Y), respectively. α is a parameter between 0 and 1, whose value will be determined later. This form yields the good barrier for decohesion ($-E_n^X$) and reasonable values for the self-surface diffusion and edge-diffusion. In order to get positive barriers for each possible process α has to be bounded between *0.3* and *0.6*. A simple exercise using Lenard-Jones type potentials on an fcc structure shows that the ratio of the energy barrier for self-surface diffusion and adsorption energy should be around *0.35*. It is immediate to realize that this ratio is exactly the value of α.

The numbers of phenomenological parameters are thus quite reduced: E_{WQ} the F deposition rate, the f_0 attempt frequency and the T thermodynamic temperature of the system. Systems with lattice sizes up to 500 x 500 were easily simulated in a few days on normal PC type computers (Pentium 4, 3.4 GHz). As will be discussed in the next section, realistic dynamics and growth statistics was obtained.

We will present in the following some qualitative results for illustrating the applicability of this simple method. As tests we study the dynamics of monolayer formation: island nucleation, growth, coalescence and phase-boundary movement.

3. Island nucleation and growth

We consider the deposition of A type atoms on a triangular surface formed by the same type of atoms. The parameter E_{AA} was fixed to *0.15 eV*, we assumed $f_0=10^{12} Hz$, the value of F was considered between *0.1-10* ML/s, temperature T was varied between *400-650* K and simulations on lattices up to sizes *512 X 512* was considered. We investigated the time-evolution of the system and qualitatively compared its statistics with experimental results. On Fig. 4 a visual comparison between experimental and simulation results is given. Experimental results are from an in-situ transmission electron microscopy experiment performed for Indium deposition on amorphous Carbon membrane in the MFA-KFKI (Budapest, Hungary) laboratories [17]. One has to be carefully while comparing the monolayer growth simulations with this experiment. In the experiment the islands are three-dimensional structures and not a simple monlayer! Islands are growing both perpendicularly on the plane and in the direction of the plane. One can expect thus only qualitative agreement. Simulation shown on Fig. 4.was performed for $T=400$ K with $F=10$ *ML*/s.

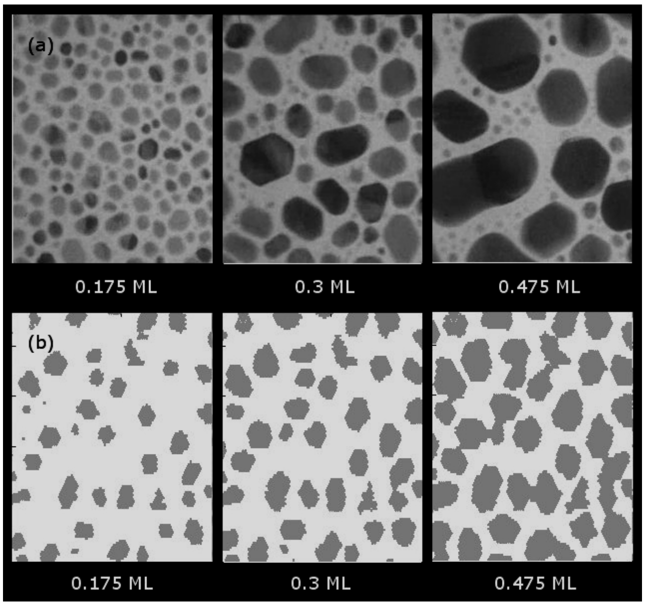

Fig.4. Visual comparison between (a) experimental and (b) simulated island-growth scenario.

The time-evolution curve of the average island size is also in qualitative agreement with the experimental one. On Figure 5. the trend for the simulated and experimental data is compared. Experimental data is from the same in-situ TEM experiment as the one presented on Fig. 4. Since experiments are for three-dimensional islands, one would expect in such case a less steep curve when the continuous layer forms. As it is observable on the figure the shape of the curves are quite similar, although the simulated curve is much steeper at the end.

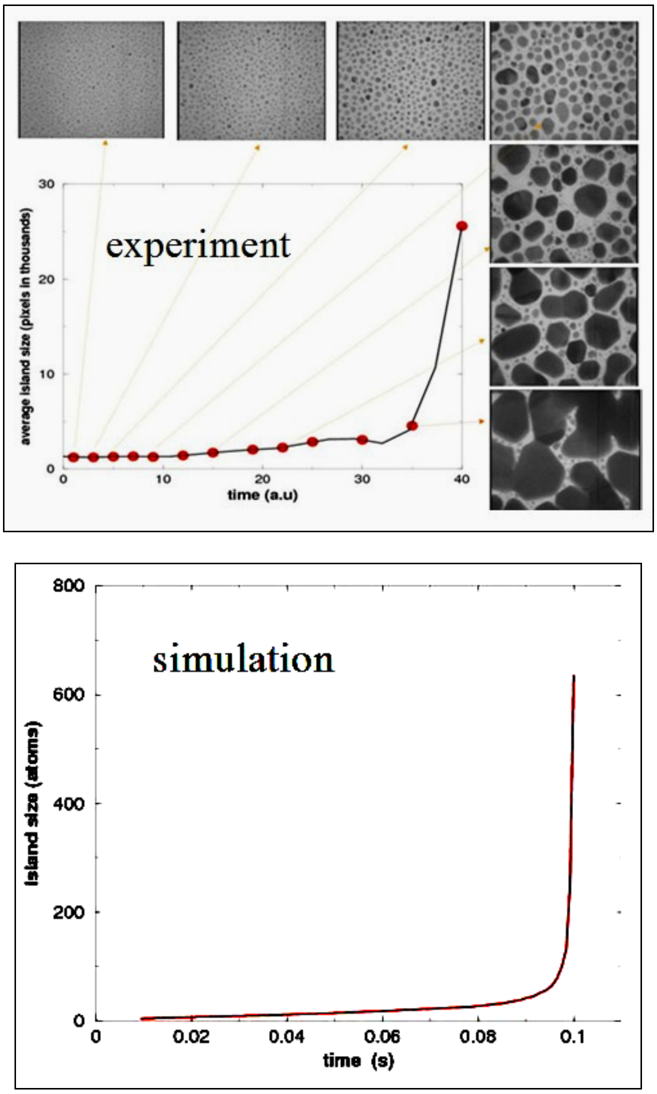

Fig. 5 Experimental and simulated trend of the average island size as a function of time during the formation of a continuous covering layer. Simulations are for T=550 K and F=10 ML/s deposition rate.

For the same filling ratio of the monolayer one can follow up the average island number in a given surface area as a function of the temperatures. As temperature increases one will have less and less islands, since the surface-diffusion process is enhanced and island growth is favored. Representing on logarithmic scale the average island number as a function of the inverse of the temperature the curve should follow the experimentally proved Arhenius-type behavior [18], i.e it should be a monotonically increasing function with a constantly decreasing slope. On Fig. 6, considering two different filling ratios in the monolayer, we present simulation results. The curves have the right trend and are in qualitative agreement with the experimental results presented in [18].

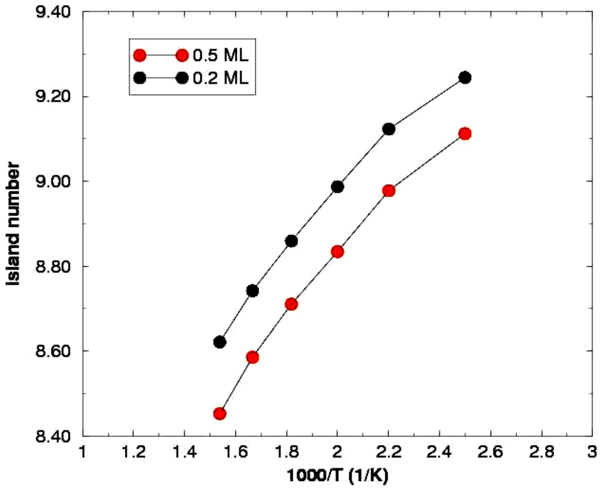

Fig. 6 Simulated Arhenius-like trend for the average number of islands in a given surface area. Simulations were performed with F=10 ML/s.

4. Evolution and annihilation of stacking-faults and phase-boundaries on an fcc (1,1,1) surface

Again, we consider the case when atoms are deposited with a fixed deposition rate (F=10ML/s) on a planar fcc (1,1,1) surface formed by the same type of atoms. Similarly with the previous case, monolayer domains of the two equivalent orientations but with different, fcc and hcp, sequences are nucleated and grown. It worst mentioning here, that although the fcc and hcp sites are geometrically equivalent the binding energy is slightly different, the fcc sites being energetically more stable. Formation, motion and annihilation of stacking faults related phase-boundaries appear and can be followed during simulation (Fig. 7). Some movies are also given on the home-page dedicated to this study [19].

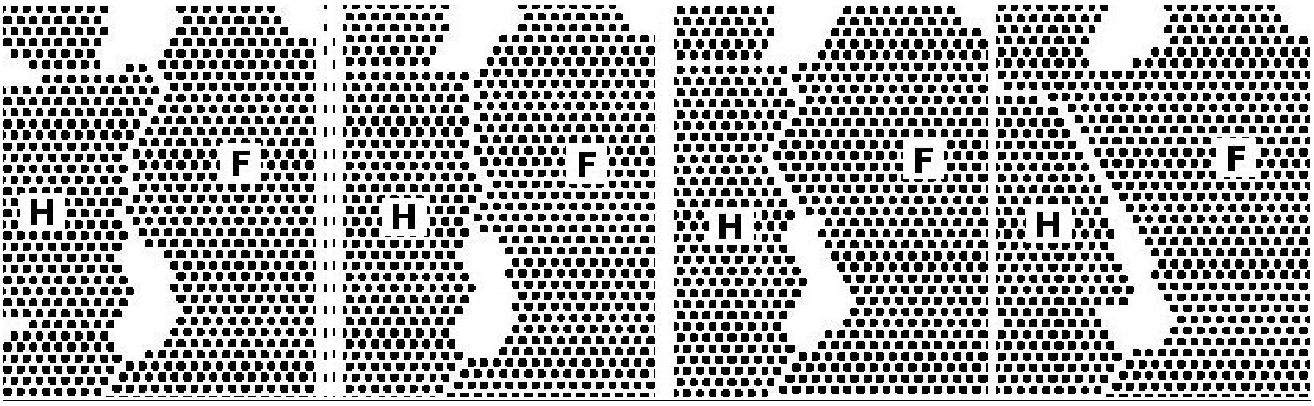

Fig.7. Characteristic time evolution and annihilation of stacking faults related phase-boundaries for the case when only A type of atoms are deposited. The pictures from left to right represent steps in the time-evolution. The F and H islands correspond to fcc and hcp stacking, respectively. Simulation parameters are: $E_{AA}=0.15eV$, *T=650K, F=10ML/s and* $f_0=10^{12}$ *Hz.*

5. Island coalescence

The scenario for islands coalescence is also in qualitative agreement with the one observed in experiments. In simulations one can observe the realistic formation of the neck and the fast rounding of the resulting islands. A simulation sequence in this sense is illustrated in Fig. 8. Movies made from simulation results are presented again on the home-page dedicated to this study [19].

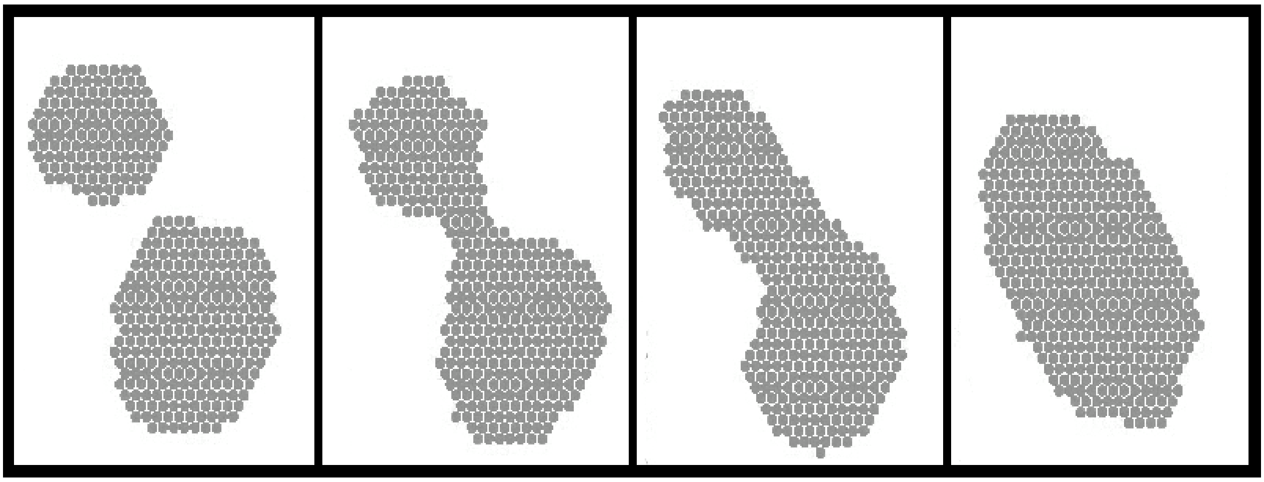

Fig. 8. Simulated island coalescence scenario. Simulation parameters are: T=450 K and F= 0.1 ML/s.

6. Conclusions

By considering a simple monolayer growth phenomenon the applicability of a novel and fast kinetic Monte Carlo method was illustrated. The method has the advantage of incorporating many degrees of freedom for the surface diffusion of the atoms and uses hopping barriers calculated from realistic pair-potentials. Island nucleation and growth, island coalescence, stacking faults and phase boundary motions are all realistic in such simulations and reproduces qualitatively well the experimental results. As shown in a recent study [18] the model works also well for the co-deposition of several types of atoms, being able to reproduce segregation patterns and structures formed during epitaxial growth. The model can be easily generalized for simulating the growth of several layers as well.

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