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MICROSCOPIC ASPECTS OF HOMOEPITAXIAL GROWTH

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Abstract

Despite the careful experimental work on the kinetic origin of the island shapes during the growth, a complete qualitative and quantitative theoretical analysis is still missing. In this paper we present the results of realistic Monte Carlo simulations of the growth of Al on Al(111). Our simulations are based on microscopic well-founded parameters derived from ab initio calculations. Reliable general criteria for interpreting the role the substrate temperature during the homoepitaxial growth on metallic fcc (111) and hcp (1000) surfaces are extracted. In particular, the importance of the asymmetry in the jump probability of fourfold coordinated adatoms and the different diffusion mechanism of the adatoms along the close–packed steps are discussed.

1. Introduction

The manipulation and the assembling of structures on the atomic scale have emerged as a feasible possibility with the developing of sophisticated Scanning Tunneling Microscopy systems [1]. That those works have already excited considerable interest is indicative of their importance for basic and applied research. However, the need of ease in building nanostructures has fostered the interest in characterizing the kinetic factors which play a role during the growth of ultrathin films. A large and outstanding experimental work (for general review see Ref. [2]) has demonstrated that to some extent structures are generated at will during growth: quantum wires and quantum dots [3], as well as pyramidal structures [4] were obtained during heteroepitaxial growth of semiconductor structures. In these cases a clear labeling of energetic and kinetic contributions is hardly achieved since elastic factors due to lattice misfit play a fundamental role [5] in determining the grown structures. Therefore, the study of the homoepitaxial growth of metallic systems seems the ideal and simplest way to pinpoint the importance of the kinetic terms, i.e. deposition rates F and substrate temperatures T_s, during the growth. Moreover, a deep understanding of their role provides

also the key to influence the growth mode and, eventually, to obtain smooth thin films: enhancement or decreasing of the substrate temperature allows or inhibits kinetic processes at the surfaces with resulting occurrence of different growth modes as well as different island shapes. Changes in the deposition rates produce transition from step flow to nucleation growth. Finally, surfactants can artificially modify kinetic mechanisms at the surface and their influence during the growth. Thus, the importance of the kinetic processes is evident and deeper insight in their role should be obtained. Detailed experimental works on this problem have been carried out [6-9] However, still this apparently simple case has not received a clear-cut theoretical picture. Recently, triggered by the development of new alghoritms, reliable calculations of the activation barriers for several mechanisms at the surface have became feasible [10], but the obtained values have not yet been cast in a form suitable for Monte Carlo (MC) simulations of the growth process. The parameters used in the previous Monte Carlo studies [11] have been always denoted as *effective* parameters without a straightforward connection with the real systems. Within this framework, despite some important qualitative descriptions, reliable quantitative information can be hardly extracted. Recently two groups have intensively employed in their simulations parameters determined by more accurate microscopic calculations based on Effective Medium Theory (EMT) [12,13]. Both simulations have been focused on Pt/Pt(111) and refer to the measurements performed by Comsa and coworkers [9,14]. However, severe doubts about these theoretical studies are in place because disagreements with the experimental data have been pointed out newly [15].

In this paper we present the results of a Monte Carlo simulation based on microscopically well–founded parameters derived from ab-initio calculations for Al on Al(111). For this system no measurements have been collected insofar, but the reliability of the input parameters enables to label general salient features behind the homoepitaxial growth of a metallic system on the fcc(111) and hcp(0001) surfaces independently from the specific material.

2. Density Functional Theory and Monte Carlo Simulations

For our simulations we employ a Kinetic Monte Carlo scheme [16,17]. In contrast to standard Monte Carlo techniques based on the Metropolis scheme where no correlation between Monte Carlo steps and real time is present, Kinetic Monte Carlo is meant to simulate the time evolution of a system of interacting particles. This implies that one considers not only the energies of the initial and final states as in the Metropolis algorithm, but also the energy (and entropy) of the intermediate states, that is, the energy barrier which separates two configurations of the system. Thus, the rates for the thermally activated processes are described by an Arrhenius form $\nu\, exp$ $(-E_B/k_BT)$ where ν is the attempt frequency, E_B the energy barrier separating the initial and final states, and T the temperature of the system. The attempt frequency contains the entropic contributions to the transitions and it could be evaluated within the framework of the Transition State Theory [18,19] provided that the activation energy is larger than k_BT. In Kinetic Monte

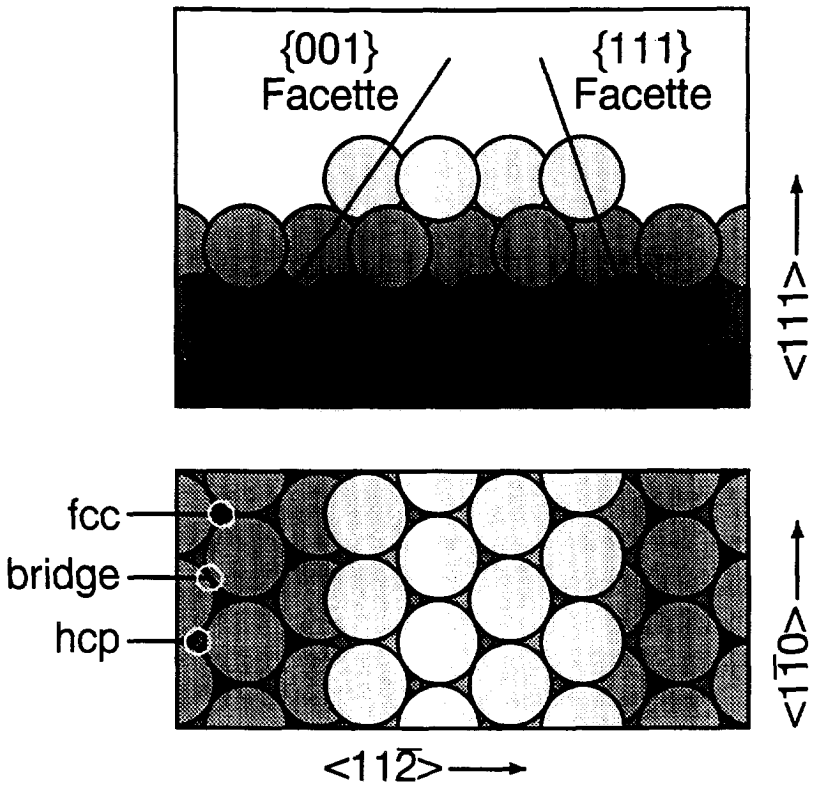

Figure 1: Side and top view of the two close–packed steps on Al(111). The three important sites for adsorption and diffusion are also indicated.

Carlo simulations of epitaxial growth the attempt frequency has usually the same value for all the processes. In this work we will demonstrate that this assumption is often not reliable.

An hexagonal lattice have been used to simulate the exact structure of the (111) surface of a fcc crystal. This is an important aspect because on the (111) surface of a fcc crystal there are two kinds of close–packed steps. The two steps are shown in Fig. 1. They differ in the orientation of their edges with respect to the substrate and they are named A and B steps, or, {100} and {111} steps, just referring to the steepest plane passing through the step edge and substrate atoms. The difference in the structure influences the diffusion of the adatoms along and through the steps, and an exact description of the (111) surface is a crucial aspect of a reliable quantitative investigation of the homoepitaxial growth. The dimension of the array represents a critical parameter of the simulation. They depend strongly on the ratio between the self–diffusion constant and the deposition rate. To avoid size effects [20] a fast self–diffusion requires very large arrays if the deposition rates are kept at values comparable with the experimental ones. In our case, because of a very low calculated barrier (0.04 eV) for diffusion of a single Al adatom on the flat (111), a (600 x 600) array has been employed. Simulations have been carried out with deposition rates of 2 and 0.08 ML/s. This latter is still larger than the typical values used in experiments, but is not unrealistic. An even smaller flux increases dramatically the computational

adatom diffusion	mechanism	E_d (eV)
flat Al(111)	hopping	0.04
{111} step $\parallel$	exchange	0.42
{100} step $\parallel$	hopping	0.32
{111} step $\perp$ desc.	exchange	0.06
{100} step $\perp$ desc.	exchange	0.08
corner jump (bridge)	hopping	0.17
corner jum (atop)	hopping	0.28

Table 1: Mechanism and energy barriers (in eV) for the relevant processes accounted for in the Monte Carlo simulations. The energy barriers are taken from Ref. [10].

cost, because a larger simulation array is required. Finally, we assume irreversible attachment of adatoms to form dimers, that is, the critical size i is equal 1.

As already pointed out, the energy parameters used in our simulations represent the output of ab initio calculations [10] base on density functional theory within the local density approximation. The details of the calculations and of the method are described in Ref. [10]. It is important to mention that a wide set of diffusion processes have been energetically well characterized in that investigation. In Table 1 we have collected the calculated energy barriers (from Ref. [10]) for the processes included in our simulations. The activation energy for the self–diffusion on the flat surface is extremely low, 0.04 eV. Comparably small are the barriers for the descending diffusion across the {100} and {111} steps (i.e., diffusion across the step from the upper to the lower terrace), 0.08 and 0.06 eV, respectively, provided that the migration takes place through an exchange process. Therefore, we expect layer-by-layer growth for substrate temperature $T \geq 25$ K. Below $T = 25$ K the activation barrier for descending diffusion from upper terraces becomes a hindrance, but at those low temperatures island edges will be frayed and fractal. This increases the attempt frequency of adatoms to migrate across the descending steps and might even reduce the barrier. Thus, we can predict layer-by-layer growth for Al on Al(111) within a wide range of substrate temperatures.

For the diffusion along the steps the activation energies are relatively large (0.32 and 0.42 eV for the {100} and {111} steps, respectively). However, the calculations shown that the energetically favoured diffusion mechanisms are the normal hopping and the exchange process for migration along the {100} step and along the {111} step respectively. This difference will play an important role in the comprehension of the island shapes.

3. Island shapes

The result of the simulations are shown in Fig. 2. Here, only $\approx 1/8$ of the effective simulation array is displayed. The coverages are always in the submonalyer regime. In Fig. 2a and b the substrate temperatures are 60 K and 80 K, respectively, and the dendritic shape of the islands is

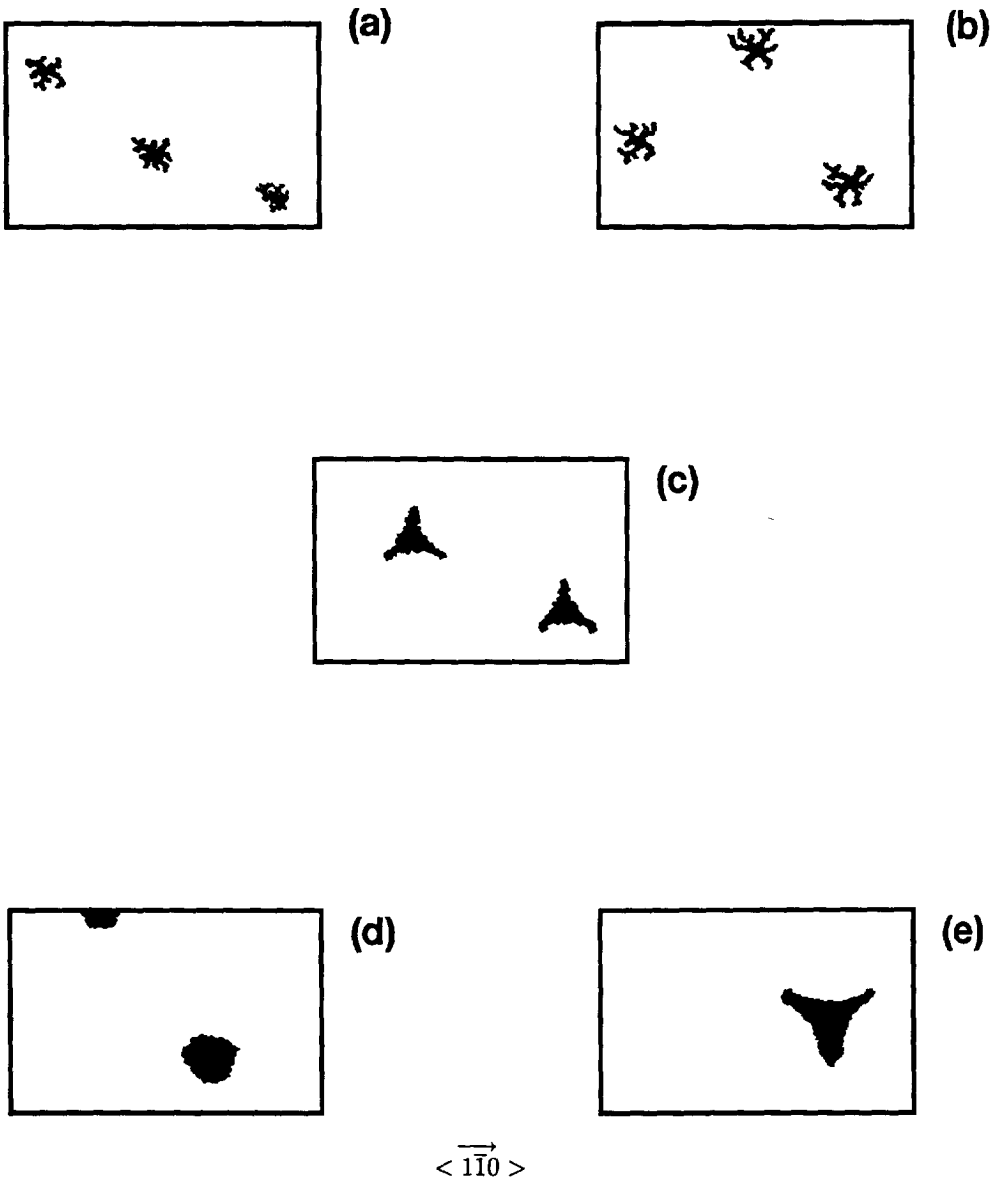

Figure 2: Section ($\approx$1/8) of the simulation array under the following growth conditions: (a) T_s = 60 K, (b) T_s = 80 K, (c) T_s = 130 K, (d) T_s = 210 K, (e) T_s = 250 K. The deposition rate is 0.08 ML/s and the coverage is Θ = 0.08 ML.

recognizable. At such a temperature most of the processes are frayed, adatoms cannot leave a step and cannot diffuse along the steps. Therefore, a kind of *hit and stick* mechanism takes place in this growth condition. At T_s = 130 K (see Fig. 2c) triangular islands can be identified which are bounded by {100} steps. Increasing the temperature till T_s = 210 K a transition from triangular to hexagonal shape occurs as can be seen in Fig. 2d and for T_s = 250 K a further transition switches on and the islands become triangular again (Fig. 2e). However, at this temperature they

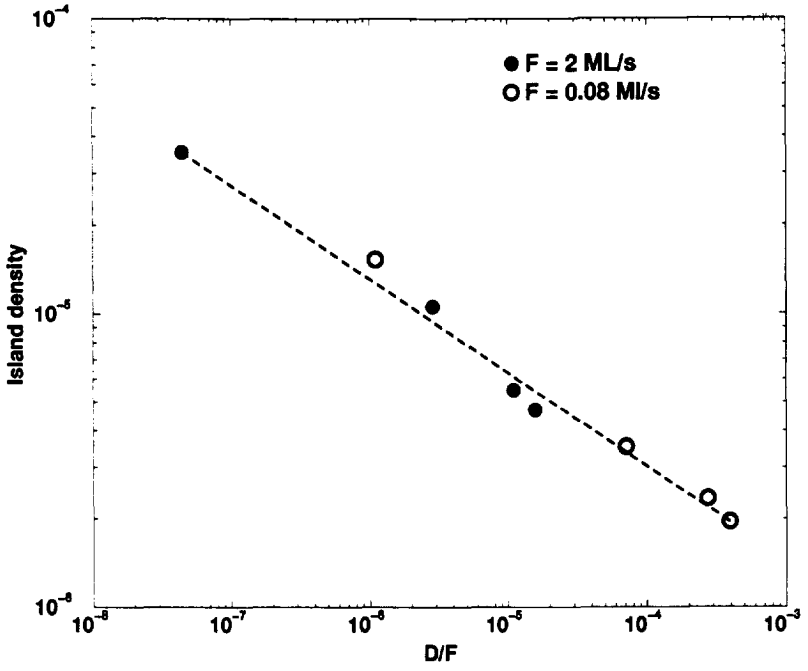

Figure 3: Island density (in cm^{-2}) versus D/F at a fixed coverage (Θ = 0.08 ML) with F = 2 ML/s (filled circles) and F = 0.08 ML/s (open circles).

are mainly bounded by {111} steps.

In Fig. 3 we report in a logarithmic plot the island density as a function of the ratio D/F where D is the diffusion coefficient for the the self migration. The slope of the straigth line fitting the simulation points is -0.32, to compare with the value of -0.33 predicted by nucleation theory in the case of $i = 1$ [21].

The very low temperature simulations require a few words. Especially at T_s = 80 K, many islands display a triangular envelope with {111} sides, while at slightly higher temperatures (T_s = 130 K) triangular shapes with {100} sides are observed. The preferential orientation of the islands at T_s = 80 K is confirmed by the fact that the total number of {111} sides is much larger than that of {100} sides. The same orientation of the envelop has been observed experimentally for Pt/Pt(111) [15] and Ag/Pt(111) [22].

The reason for this behaviour lies in an asymmetry in the probability of thermally activated diffusions of atoms which are stuck at a corner of an island. From the calculation of Stumpf and Scheffler [10] we estimate that an atom which is fourfold coordinated (three from the substrate and one from the island) jumps toward a fivefold coordinated position easier via a bridge position (solid line in Fig. 4) than via the atop sites (dashed line). The respective energy barriers are 0.17 eV and 0.28 eV. This has the consequence that the resulting aggregate is oriented parallel to the {111} facet. This mechanism has been recently confirmed by a low temperature Kinetic Monte Carlo simulation of Hohage *et al.* [15] which reproduces the STM images for Pt on Pt(111). These results and the experimental measurements are at odd with the previous simulations of Jacobsen

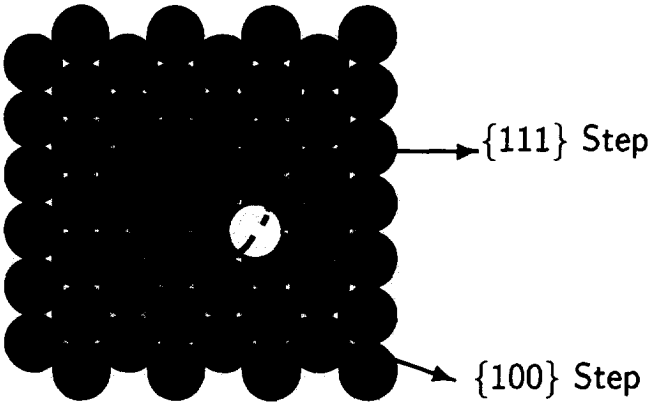

Figure 4: Schematic view of the corner effect. The dashed and solid lines indicate jumps toward fivefold coordinated places via ontop and and bridge positions, respectively.

et al. [13] which yielded low temperature fractal islands with a {100} envelop. This discrepancy should be attributed to the fact that at the corner a reversal asymmetry has been assumed: the easiest jump is via the atop site.

To understand the form of the islands in the temperature regime between 130 and 250 K we should consider the mobility of the adatoms along the steps: The lower the speed of migration along a given step edge, the higher the speed of advancement of this step edge. Thus, this step edge disappears. Since the diffusion along the dense packed steps on the (111) surface, the {100} and {111} facets, is faster than along steps with any other orientation, the criterion explains the presence of islands which are mainly bounded by {100} or {111} steps. The same argument can be applied for the triangular islands at $T_s = 130$ K. The energy barrier for the diffusion along the {111} facet is larger than that governing the migration along the {100} step edge, thus this latter survives and triangular islands with {100} sides are obtained. By considering the energy barriers we would expect only these islands, until the temperature regime for the thermal equilibrium is reached. However, the diffusion of adatoms is not entirely governed by the energy barrier but also by the prefactor. A general assessment about the values of these prefactors has not been obtained theoretically and experimentally, but it is well accepted that exchange and hopping mechanisms have different prefactors. The data reported in the literature for these two different migration processes can differ for more than two order of magnitude. The results shown in Fig. 2 are obtained with the following prefactors for the main processes: 2×10^{-4} cm^2/s for the diffusion on the flat surface, 5×10^{-4} cm^2/s for the jump along the {100} step and 5×10^{-2} cm^2/s for the exchange along the {111} step. They are estimated as weighted averages of the data found in the literatur for the same steps on metallic systems.

The difference between the prefactors for the exchange and the hopping is remarkable and

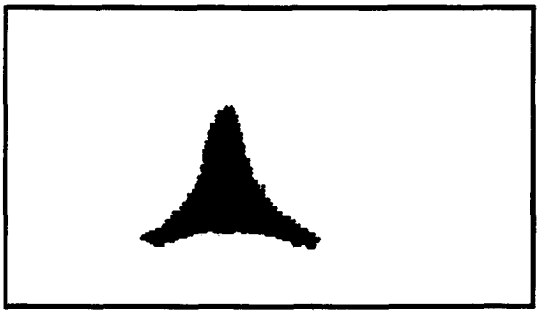

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Figure 5: Section of the surface at $T_s = 270$ K with F = 0.08 ML/s. The prefactor for the diffusion along the {111} step is 5×10^{-3} cm^2/s.

cannot be neglected. At $T_s = 250$ K the prefactors govern the diffusion along the steps which results faster along the {111} facet than along the {100} one. Thus, this latter disappears and only triangles with {111} sides are present. At lower temperature the energy barrier dominates the process and the diffusion along the {100} step becomes faster. This explains the presence of islands with {100} sides at this temperature. In this way the hexagonally shaped structures observed at $T_s = 210$ K results from the equal advancement speed for the two steps at that temperature. Indeed, with the values used in the simulations the diffusion coefficients for the adatom migration along the two steps as a function of the temperature cross at $T_{cross} = 240$ K, in good agreement with the result of our simulations. The previous argument is pivoted crucialy on the value of T_{cross}. In Fig. 5 we show the result of our simulation with a difference of one order of magnitude between the two prefactors ($D_{0\|}^{\{111\}} = 5 \times 10^{-3}$ cm^2/s vs. $D_{0\|}^{\{111\}} = 5 \times 10^{-4}$ cm^2/s). All the other parameters are kept at the same values than the previous simulations. In this case, T_{cross} lies in the regime where thermal equilibrium is set and the {111} step-triangles do not appear. Only {100} step-triangles are present and this demonstrates the importance of the prefactors for a deep comprehension of island shapes during the growth: A difference of two orders of magnitude can produce the transition between the triangular islands. In several cases differences of the same order of magnitude between experimentally determined prefactors for exchange and hopping prefactors have been determined.

In conclusion, we have presented the results of a complete investigation on the influence of the substrate temperature on the island shape during the growth of Al on Al(111). The energy barriers for the considered processes at the surface have been determined via ab initio calculations and are not effective parameters. We have pointed out the important role of the asymmetry in the jumps at the corners for fourfold coordinated adatoms in determining the particular orientation of the fractal islands at low temperatures. For the transition of the orientation of the triangular

islands the driving mechanism has been identified in the different migration process which characterizes the diffusion along the two close–packed steps. Obviously, the next step in this investigation will be a direct evaluation of the prefactors for the normal jump and the exchange process. Work in this direction is in progress.

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