Linköping Studies in Science and Technology
Licentiate Thesis No. 1830

Víctor Gervilla Palomar

Metal film growth on weakly-interacting substrates

Stochastic simulations
and analytical modelling

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Linköping, 2019

The cover image shows two faceted 3D islands grown on a weakly-interacting substrate, coming into contact to start a coalescence process. Island growth and coalescence were simulated with the software Uni_KMC (Bo Lü), and simulation outputs were visualized with the free-software Ovito.

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Abstract

Thin films are nanoscale layers of material, with exotic properties useful in diverse areas, ranging from biomedicine to nanoelectronics and surface protection. Film properties are not only determined by their chemical composition, but also by their microstructure and roughness, features that depend crucially on the growth process due to the inherent out-of equilibrium nature of the film deposition techniques. This fact suggest that it is possible to control film growth, and in turn film properties, in a knowledge-based manner by tuning the deposition conditions. This requires a good understanding of the elementary film-forming processes, and the way by which they are affected by atomic-scale kinetics. The kinetic Monte Carlo (kMC) method is a simulation tool that can model film evolution over extended time scales, of the order of microseconds, and beyond, and thus constitutes a powerful complement to experimental research aiming to obtain an universal understanding of thin film formation and morphological evolution.

In this work, kMC simulations, coupled with analytical modelling, are used to investigate the early stages of formation of metal films and nanostructures supported on weakly-interacting substrates. This starts with the formation and growth of faceted 3D islands, that relies first on facile adatom ascent at single-layer island steps and subsequently on facile adatom upward diffusion from the base to the top of the island across its facets. Interlayer mass transport is limited by the rate at which adatoms cross from the sidewall facets to the island top, a process that determines the final height of the islands and leads non-trivial growth dynamics, as increasing temperatures favour 3D growth as a result of the upward transport. These findings explain the high roughness observed experimentally in metallic films grown on weakly-interacting substrates at high temperatures.

The second part of the study focus on the next logical step of film formation, when 3D islands come into contact and fuse into a single one, or coalesce. The research reveals that the faceted island structure governs the macroscopic process of coalescence as well as its dynamics, and that morphological changes depend on 2D nucleation on the

facets. In addition, deposition during coalescence is found to accelerate the process and modify its dynamics, by contributing to the nucleation of new facets.

This study provides useful knowledge concerning metal growth on weakly-interacting substrates, and, in particular, identifies the key atomistic processes controlling the early stages of formation of thin films, which can be used to tailor deposition conditions in order to achieve films with unique properties and applications.

Preface

The present thesis is part of my Ph.D studies at the Nanoscale Engineering Division in the Department of Physics, Chemistry and Biology of Linköping University. The goal of my research is to contribute to the understanding of the elementary processes and the dynamics of thin metal film and nanostructure formation on weakly-interacting substrates. This research is financially supported by the Swedish Research Council (Vetenskapsrådet, VR-2015-04630) and Linköping University. Research results are presented in three appended papers, preceeded by an introduction to the scientific field and research methods.

Víctor Gervilla Palomar

Linköping, December 2018

Appended papers and contributions

1. “Formation and morphological evolution of self-similar 3D nanostructures on weakly-interacting substrates”

B. Lü, G.A. Almyras, V. Gervilla, J.E. Greene and K. Sarakinos, *Phys. Rev. M.* 2, 063401 (2018)

I contributed to the upgrading and validation of the simulation code, performed the simulations and analyzed the data.

2. “Dynamics of 3D-island growth on weakly-interacting substrates”

V. Gervilla, G.A. Almyras, F. Thunström, J.E. Greene and K. Sarakinos, *Phys. Rev. M*, under review (2018)

I contributed to the design of, I conceived and developed the analytical model proposed in the article. I designed the simulation method and discussed the simulation results. I wrote the manuscript.

3. “On the dynamics of surface-diffusion-driven nanoscale coalescence”

V. Gervilla, G.A. Almyras, B. Lü and K. Sarakinos, *manuscript in final preparation* (2019)

I contributed to the design of, I performed the simulations, analyzed the data, and formulated the analytical model presented in the manuscript. I wrote the manuscript.

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1 Introduction

1.1 Motivation

The term *thin film* refer to any layer with thickness ranging from a single atomic layer up to several micrometers [1]. Thin films have become an ubiquitous element [1,2] in science and technology, since their low dimensional features allow to explore new physical phenomena, as well as to design materials and devices able to adress challenging technological objectives. They are used, for instance, to study novel properties exhibited by matter when the motion of electrons is confined in two dimensions, as in the quantization of electrical conductance [3,4] or in superconductivity [5]. On the technological side, their applications range from pure decorative purposes to functional coatings, including highly reflective [6], as well as corrosion [7] and thermally [8] resistant coatings. One common aspect that thin films share is the modification of the physical properties of their constituents compared with their bulk counterparts, due to the constraint to small length scales. Thus, for instance, it is possible to enforce immiscible materials to form metastable alloys [9,10], impose different film atomic structures by the use of specific substrates [11], or modify the band-gaps of materials by adjusting film strain [12,13,14].

Thin film research branches into two main categories: study of *epitaxial growth*, the scenario in which the crystalline structure of the substrate imposes an order upon the structure of the deposit, and study of *non-epitaxial growth*, for which no long-range structural correlation exists between substrate and deposit. In addition, if the substrate has identical chemical composition than the deposit material, the system is said to be *homoepitaxial*, otherwise it is said to be *heteroepitaxial*. A large body of knowledge has been obtained for epitaxial systems, and in particular, for metal-on-metal homoepitaxy as a model system, whose simplicity allows to distinguish between kinetic and thermodynamic effects on the growth morphology. However, many thin film technologies require deposition of material on non-epitaxial substrates, such as amorphous surfaces or surfaces whose lattice parameter differs greatly from that of the deposit. When materials interact weakly with the substrate, they tend to dewet and form three-dimensional (3D) nanostructures, which, in case they are supported by a polycrystalline or amorphous substrate, grow with random orientations—note that non-

epitaxial growth is not a necessary condition for materials on weakly-interacting substrates, check e.g. Au, Ag and Cu growing epitaxially on mica [15,16,17]. Eventually, randomly oriented nanostructures come into contact and coalesce, yielding polycrystalline films with properties which may differ drastically from those of the bulk solid. This observation indicates that film properties are not only determined by their chemical composition, but also by their morphology and microstructure, which is highly dependent on the synthesis technique and conditions.

The most widely used method for synthesizing films is *physical vapor deposition* (PVD) [18], in which solids are vaporized and their atoms are transported through a gas phase toward a substrate, where the atoms adhere and subsequently aggregate forming the films. Due to the high arrival rate of atoms to the substrate, growth is mainly controlled by kinetics [19,20], i.e., the individual atomic events occurring at the surface, and therefore the final features of the film might be completely different to those obtained if the film could relax toward thermodynamic equilibrium. Substantial effort has been devoted to understand the influence that kinetic effects have on thin films and nanostructures, owing to the demand of the electronics industry for miniaturization of components [21,22], and to the need of improving effectivity of energy generation and storage [23], among others. Thus, by finding correlations between atomistic mechanisms and film growth stages, we may open the way for the design in a knowledge-based way of a wide range of technologically important materials.

1.2 Research goal & strategy

In this thesis, I direct my efforts to study, theoretically, growth of thin metal films and nanostructures on weakly-interacting substrates, specifically Ag on SiO₂. This is crucial for understanding extended experimental knowledge that my present and former colleagues at the Nanoscale Engineering division have generated over the past years [24,25]. The focus on this particular deposit/substrate system is due to its applicability on in diverse relevant technologies. To name a few, it can be used to produce energy-saving windows [6], to improve the turnover frequency on catalysis [26], to construct sensors useful in biomedicine [27,28], and to enable 2D materials in new-generation nanoelectronic devices [29,30].

To give a strict definition of a *weakly-interacting substrate* is not a trivial task, since the interaction between the substrate and the film depends on the particular material deposited—e.g., Pb interacts weakly with graphene, while Dy is strongly bounded to it [31]—and the tendency for the islands to become 3D depends to some extent to the substrate temperature [32]. For this reason, Campbell [33] suggested to define a film/substrate system as weakly-interacting, when the interatomic bond strength between a film and a substrate atom is at least half of the bond strength between two film atoms.

At present, the early stages of film growth on weakly-interacting substrates remains only partially understood. Current knowledge mostly concerns epitaxial systems [19] where islands adopt two-dimensional (2D) profiles, which is of little use to study growth of metals on weakly-interacting substrates, as in this case material has the tendency to form pronounced 3D structures [34]. Growth of noble metals, together with Fe and Pb, on TiO₂, SiO₂ and MoS₂ [35-42], for instance, has been experimentally characterized, but these results do not necessarily match theoretical predictions from mathematical and computational models (see Section 2.4). The reason for the discrepancy is that models of film growth dynamics are based on predictions of thermodynamic theories [43-47], which do not account for the *out-of-equilibrium* nature of deposition processes, and also that the non-trivial morphological features on the films are neglected (e.g., 3D nanostructures on surfaces are approximated to spheres [48]). Thus, the atomistic origin of nanostructure morphologies and the way by which they determine subsequent stages of film growth remain poorly understood. This thesis is, therefore, oriented to contribute to the current knowledge about the synthesis of metal thin films on weakly-interacting substrates, by means of atomistic *kinetic Monte Carlo* (kMC) simulations of single island growth and coalescence. Simulation results are combined with analytical models based on diffusion equations, and are also compared with predictions from thermodynamic nucleation theory. The above-mentioned computational and analytical models help to connect the available information on surface dynamics with the characteristic microscopic processes responsible of growth, contributing in this way to answer the fundamental question in materials science, i.e., how the microscopic processes determine the macroscopic evolution of a given material system. Furthermore, they may provide useful information

for the design of strategies to modify and control growth by manipulating its underlying kinetics, such as depositing material using vapor pulses [49] or adding surfactants to the substrate [50,51].

Chapter 2 starts with a description of the essential aspects and stages of thin film growth, where weakly-interacting substrates are discussed. Then chapter 2 continues with a discussion on the formation and morphology of 3D nanostructures and coalescence. In Chapter 3, the physical model implemented in our simulation code is described, along with a review of the kMC method, its assumptions, requirements, and limitations. Chapter 4 describes the theoretical foundations of the mathematical model developed to study single-island morphology dynamics. A summary of the appended papers is given in Chapter 5, followed by a brief discussion on the future direction of the research topics in this thesis in Chapter 6. Finally, a last section in Appendix is devoted to the parallel versions of the kMC codes.

2 Thin film growth

2.1 Thin film growth stages

Regardless of the specific technique used, every film growth experiment starts from the deposition of material onto a substrate. Once atoms are on the substrate, they are said to be *adatoms*, and they diffuse until they meet another adatom, or a low energy position on the surface, to nucleate and form islands. For near-to-homoepitaxy systems, islands keep a nearly 2D morphology and are confined under the same lattice, as this is imposed by the crystalline structure of the substrate, whereas for weakly-interacting substrates, islands exhibit prominent 3D morphologies, which, due to the low attraction from the atoms underneath, are able to migrate over the substrate—for island sizes up to a certain threshold [52,53]—and may be randomly oriented in case the substrate is polycrystalline. Once a certain density of islands is covering the substrate, adatoms will inevitably incorporate to already-existing islands instead of nucleating new ones, hence this density saturates to a constant value

$$N_{sat} \sim \left(\frac{F}{D}\right)^\chi, \quad (2.1)$$

depending on the *deposition flux* F and the surface *diffusivity* D . χ is an exponent that depends on the dimensionality of the islands.

When two or more islands come into contact and form a cluster, they undergo an equilibration process by surface diffusion, or *coalescence*, striving to reach the compact shape with the lowest energy possible. Possible differences in crystallographic orientation between 3D islands cause grain boundaries to form between them upon impingement, which are expelled from the coalescing cluster via atomic rearrangement of both sides of the boundary. The main consequence of coalescence is that, after the *island saturation density* (Eq. 2.1) has been reached, the mass redistribution of clusters uncovers portions of the substrate that were previously covered by the islands. Since the total surface coverage decreases, new nucleation events on the substrate may occur and give rise to a second generation of islands. However, the rate at which islands come into contact eventually surpasses the rate of cluster coalescence, and new islands start impinging on the clusters before they have

completed their equilibration. In this way, clusters acquire increasingly elongated shapes, and they soon collapse into a single network spanning the entire surface¹. Material deposited from this point contributes to increase the average thickness of the film, which, after the substrate regions not covered by the percolated structure are filled, becomes continuous. It is worth to note that the process of hole filling is not trivial and may take considerable amounts of time, specially at low temperatures, due to the Zeno effect [54,55] (Section 2.3).

Continuous films may present a variety of microstructures depending on the way by which islands grow initially and the rate by which they coalesce, among other factors. Thus, in epitaxial systems islands tend to grow with the same orientation, which results in films formed by a single crystal structure with defects such as misfit dislocations, domain boundaries and twins, whereas, for non/epitaxial systems, the random orientation of islands give rise to polycrystalline films with grains separated by boundaries. Because of their large impact on the final features of films, in this thesis I focus my research specifically into the initial stages of the film growth process, namely 3D island formation and coalescence, and attempt to understand their dynamics and the way by which they are governed by individual atomistic mechanisms. For this reason, I provide a more detailed background of these two stages in Sections 2.3 and 2.4.

Although film growth proceeds far from equilibrium, use of thermodynamic arguments is instructive for understanding trends with respect to film morphological evolution. This was done by Bauer in 1958 [56] using the energy balance between the surface free energy γ_S of the substrate, the surface free energy γ_D of the deposit, and the interfacial free energy² γ_{int} . For the case

$$\gamma_S < \gamma_D + \gamma_{int} \quad (2.2)$$

¹ This transition known as percolation is, particularly, easy to measure experimentally for metals on insulating substrates, since the film becomes electrically conducting.

² Thermodynamic minimization principles requires that the ratio between each of the areas of the system is such that the total free energy reaches its minimum possible value.

Figure 1. Classification of epitaxial growth modes according to Bauer, in which a) corresponds to Volmer-Weber growth, b) to Frank-van der Merwe growth and c) to Stranski-Krastanov growth.

the energy balance requires to minimize the area covered by the deposit, which is driven to agglomerate into 3D nanostructures. This mode is known as *Volmer-Weber growth* (Fig. 1.a). On the other hand, if

$$\gamma_S \geq \gamma_D + \gamma_{int}, \quad (2.3)$$

the deposit will tend to cover the substrate to maximize the interface area vs. the substrate area, leading to *Frank-van der Merwe* mode (Fig. 1.b). In this growth mode, thin films form by consecutive aggregation of layers of one-atom thicknesses (i.e., monolayers), and is mostly found in purely and approximately homoepitaxial systems³. If Eq. (2.3) holds for a material with a significant lattice mismatch with the substrate, as layer-by-layer growth proceeds the elastic energy resulting from the lattice mismatch will build up, and contribute to the γ_{int} of the top layers and the newly-deposited material. After deposition of a certain amount of material, this progressive accumulation of elastic energy will inevitably lead to a reverse of condition (2.3) into condition (2.2), and the material will tend to form dispersed 3D islands in order to release the strain energy, an scenario known as *Stranski-Krastanov mode* (Fig. 1.c). Nevertheless, the transition from 2D to 3D islands is not the only mechanism allowing the film to release strain energy; generally, for low temperatures and low lattice-

³ In a purely homoepitaxial system, $\gamma_{int} = 0$ and $\gamma_D = \gamma_S$ by definition.

parameter mismatch, this can also be achieved by the generation of missfit dislocations and maintaining the 2D growth mode [57].

It is important to point out that the Bauer classification is exclusive for near-to-equilibrium epitaxial systems, since it assumes that relaxation towards free energy minimums is possible. Concurrently, all deposition techniques are fundamentally out-of-equilibrium processes, and kinetic effects dominate or are an important component of film growth; as material is continuously added to the surface, the system is impeded to reach thermodynamical equilibrium, and instead it evolves to metastable configurations associated with local minima of the energy landscape. One well-known example of this situation is the shape of snowflakes, which nucleate in changing atmospherical conditions and, as a result, appear in countless forms [59] (Fig. 2), while rigorously there is an unique equilibrium configuration for a given number of water molecules.

Figure 2. Several metastable shapes for ice crystals grown at different ambient conditions [60].

In the same way, the possibility of controlling the deposition conditions in growth experiments allows to synthesize films with a vast variety of morphological features and their correspondent properties for the same material system. Understanding the way by which films and nanostructures are influenced by the deposition conditions thus requires viewing out-of-equilibrium growth as the collective effect of the individual atomistic events taking place on the film/substrate system. This knowledge opens up the possibility of controlling film growth by adjusting deposition parameters, and in turn modifying the kinetics of the process. A good example of the way by which kinetics can be affected by deposition parameters is the growth of monolayer islands with different morphologies on homoepitaxial systems, such as Ag/Ag(111) or Pt/Pt(111) [61,62], where their shapes transition from dendritic to compact upon a growth temperature increase.

2.2 Nucleation

While there are several deposition methods to grow thin films, in this work we focus on PVD, in which material is vaporized and transported through the gas phase toward a substrate. Upon arrival, atoms transfer to the substrate a part of their kinetic energy, which is dissipated in form of lattice vibrations, and then diffuse over the surface until they find other atoms to nucleate a new layer, or stable positions to attach to. From a thermodynamic perspective [63], nucleation occurs due to a difference $\Delta\mu$ between the chemical potential of the vapor phase and the chemical potential of the substrate, which drives the system to incorporate vapor atoms into the bulk of the substrate in order to minimize the total energy. $\Delta\mu$ can be calculated from the Gibbs-Thomson equation

$$\Delta\mu = k_B T \ln\left(\frac{P}{P_0}\right), \quad (2.4)$$

where P is the pressure of the vapor phase and P_0 is the *equilibrium vapor pressure*, i.e., the pressure at which mass transfer occurs at the same rate in both directions between the solid and the vapor phase. The ratio P/P_0 is referred as *supersaturation*, which is useful to account how far is the interface of the phases from equilibrium conditions.

Figure 3. Plot of the free energy variation $\Delta G(p) = 2\gamma_{line}\sqrt{\pi p} - p\Delta\mu$ of a surface after the formation of a nucleus of p atoms, as a function of p . This variation reaches a maximum value ΔG^* for a critical nucleus formed by p^* atoms.

For a gas atom to become part of the bulk, once it has been deposited it needs to meet with other atoms to form a stable nucleus of p atoms. The formation requires the system to spend an energy $2\gamma_{line}\sqrt{\pi p}$ for building a vapor/solid interface, where γ_{line} is the line tension of the nucleus, but at the same time it gains an energy $p\Delta\mu$ by bringing the atoms together from the vapor phase. Thus, the free energy change associated to the formation of the nucleus (Fig. 3) becomes

$$\Delta G(p) = 2\gamma_{line}\sqrt{\pi p} - p\Delta\mu. \quad (2.5)$$

This function reaches a maximum ΔG^* value at $p^* = \pi\gamma_{line}^2/\Delta\mu^2$, which constitutes the *critical size* of the nucleus. Once the latter is formed, it tends to evolve according to the free-energy minimization principle; if $p < p^*$, the nucleus will tend to decrease in size and disappear, since this would lower the total energy of the system, while if $p > p^*$, the energy will be lower by making the nucleus grow. For the case of $p = p^*$, whether the nucleus disappears or survives and grow depends on random thermal fluctuations of its environment. Eqs. (2.4) and (2.5) are used in Paper 3 to estimate

quantitatively the nucleation rate on the facets of a pair of islands undergoing a coalescence process (see Section 2.4).

The previous treatment does not include any information related with the atomic diffusion, which, since deposition is an out-of-equilibrium process, plays a fundamental role for the evolution of the film and therefore must be accounted for. If the surface is at temperature well below the melting point of the material, a continuous diffusion pathway can be decomposed in a discrete series of jumps between neighbouring adsorption sites. A transition between two adjacent sites requires that the atom breaks the energy bonds with his surrounding neighbors, and move through a path of increasing energy until it feels the attraction of the atoms around the final site. The potential energy experienced by a diffusing atom at each point of the surface defines a function known as *potential energy landscape* (Fig. 4), whose local minima or *basins* correspond to adsorption sites, and each point of the landscape where an atom transitioning between sites reaches the highest energy is called a *saddle point*. Thus, the potential energy difference between the initial site and the saddle point, constitutes an *energy barrier*⁴ E_a that the atom must overcome in order to transition between sites

Figure 4. Schematic representation of the energy landscape associated to a surface. E_a is the energy barrier correspondent to a diffusion jump between two adjoining sites on a flat surface.

⁴ This quantity is also referred as activation barrier or activation energy.

successfully, and determines the average rate v at which these jumps take place. The two quantities follow an exponential dependence given by the Arrhenius equation,

$$v = v_0 e^{\left(-\frac{E_a}{kT}\right)}, \quad (2.6)$$

where v_0 is the Debye frequency of the solid beneath, T its temperature, and k the Boltzmann constant.

To complete the description above, and make possible the identification of different diffusion processes, a characterization of the most common features of a crystalline surface is required, which we do by using the classically accepted step-edge-kink model (Fig. 5) [64]. Atoms are adsorbed on a flat empty surface, called a *terrace*, and form new layers, or *islands*, bounded by *edges*. The intersection between two edges is called *corner*. Edges may be disrupted by *kinks*, which consist on single-atom-width displacements of the edge. As mentioned above, the easiness atoms have to diffuse is dependent on the number of bonds they have to break in their jumps, and thus the hierarchy of process rates can be roughly inferred from the morphological features previously discussed. Diffusion through a terrace is the most frequent process, as the atom only distances slightly from its neighbours below before feeling the attraction of those in the final position. Along the same lines, edge diffusion proceeds easily, but only along ideal edges formed by straight lines of atoms; rounding a corner requires the atom to take a considerable distance from its initial neighbors in order to reach the saddle point, and thus it occurs at lower rates. It follows that detachment from edges

Figure 5. Schematic visualization of a surface depicted by the step-edge-kink model.

and kinks, where a bond is broken but there is no attraction from an atom in a similar position on the final state, become the most unfrequent processes on this model⁵.

2.3 Island growth

When an edge is regarded as the boundary between terraces at different height, it is instead called *step*. Atomic diffusion across steps deserves a separate discussion, since this single process regulates the roughness of the growth front of films and hence it is of particular interest in the study of micro- and macroscale connection. The atomistic pathway to follow for crossing a step downward, from a terrace to the edge position below, is considerably longer than for other processes and for this reason its correspondent energy barrier is larger and is difficult to estimate by mere bond counting. The additional energy arising from the extra length of the diffusion jump is known as *Ehrlich-Schwobel barrier* or *step barrier* [67-71]. This barrier associated with atom descent limits the interlayer mass transport between the top of flat islands and the substrate, and, in the same way, in a percolated film limits the transport between the most exposed regions and the bottom of the holes of the film (Zeno effect) [54,55].

As this energy barrier regulates material transport between atomic layers on the surface, it can be used to illustrate how the modification of deposition conditions in out-of-equilibrium film-growth processes allows to influence and control the final film features; upon deposition of material on a substrate, small single-layer islands start forming, whose perimeters are bounded by a step with an associated step barrier. This implies that any atom directly deposited on top of an island must overcome this barrier in order to diffuse down to the substrate, a process which, according to the Arrhenius equation (Eq. (2.6)), will occur more often if the temperature is higher. From this follows that for a deposition experiment, if temperature is sufficiently large for atoms to overcome step barriers and escape the island tops, layer-by-layer growth occurs. Otherwise, atoms are confined within island tops, where they eventually nucleate new

⁵ Extense lists of energy barriers for surface diffusion processes have been calculated for metal-on-metal homoepitaxial systems [65,66], e.g., Cu/Cu(100) and Ag/Ag(111), based on the coordination numbers of initial and final positions (see Section 3.3).

layers and the islands evolve to 3D stepped structures or *mounds*. The process of gradual switch between these two resulting film morphologies is known as *kinetic roughening*, and is a good example of how growth does not necessarily proceed as prescribed by the thermodynamic rule of energy minimization.

Interestingly, for weakly-interacting substrates, islands tend to adopt pronounced 3D morphologies. It is known that they form already at the very initial stages of film growth, as measurements of surface coverage after deposition of small amounts of material [72] reveal that only a fraction of the deposit is in contact with the surface, and the fact that these islands are still too small to efficiently capture atoms from the vapor phase indicates that some upward transport mechanism is involved in their formation. The most intuitive explanation is that the atomic bond between a film and a substrate atom is much weaker than the bond between two film atoms, edge atoms are allowed to cross the step barrier in the opposite direction and ascend to the island top from the substrate—this is a very unlikely process in homoepitaxy—and in this case a high temperature favors 3D growth [73], in contrast with the previous example. However, the concept of step barrier can only explain partially the formation of 3D islands on weakly-interacting substrates, which in addition exhibit a morphological evolution radically different than that observed in near-to-homoepitaxial film/substrate systems; this picture does consider that, once atoms are on top of the second layer of an island, they are bounded to atoms of their same type below and therefore a further ascent becomes, at best, improbable. Thus, although the step crossing mechanism suffices to explain roughness changes in near-to-homoepitaxy systems [69], it cannot account for the pronounced 3D island morphologies observed on weakly-interacting substrates [34], which might be explained by a complementary atomistic process. A hint that could shed some light on this question is the difference between the surface features of 3D islands grown in homoepitaxial and weakly-interacting substrates: while in the former case the island sides are formed by stepped surfaces [74], in the latter case the sides might be smooth facets [75], which, for a diffusing atom, mimic the environment experienced when crossing a flat terrace. This is a feasible explanation to the origin of the 3D island, but yet there is no agreement on whether it indeed occurs in this way or not. In addition, the concept of step-edge barrier constitutes a kinetic limitation which alone determines the final morphology of islands grown on homoepitaxial systems

depending on temperature, but there is no known equivalent process responsible of the 3D island morphologies. These questions are explored through kMC simulations and a diffusion-equation-based analytical model in Papers 1 and 2.

2.4 Island coalescence

From a mesoscopic point of view, coalescence is arguably the crucial stage of growth determining the final features of a nanostructure or a film, as the density of grain boundaries and roughness are dependent on the rate at which two or more islands merge upon contact⁶ [20,76,77,78]. For deposition conditions favouring high coalescence rates, all islands covering relatively large substrate areas will eventually impinge on each other and become single crystalline structures, resulting in a substrate with a small density of large islands capturing any small island nucleating nearby. This scenario is commonly referred as droplet-growth mode. Hence, the deposited material evolves into a rough polycrystalline film consisting on large bulk regions separated by few grain boundaries. In contrast, deposition conditions inhibiting coalescence result in multiple small grains forming a dense network of grain boundaries. In this case, as percolation occurs much earlier if coalescence is slow, the constituent islands are still small when their individual growth is halted, which results in smoother films compared to those grown at conditions of large coalescence rates.

From the discussion above, it is easily inferred that an understanding of the coalescence process, as well as of the variables that it depends on, is required in order to make possible the prediction and control of nanostructure and film growth. The problem of two solids redistributing their material to become a single one was first undertaken while developing the sintering theory in the 1950's [43,46,47]. The range of temperatures treated by these studies spans up to values close to the melting point of materials, and consider several mechanisms of mass transport such as viscous flow or bulk diffusion, although for deposition experiments material is assumed to redistribute mostly by surface diffusion. Specific research of the latter case by Herring

⁶ Coalescence may also occur without island contact via mass diffusion directed from small to large islands, a process known as Ostwald ripening, which we do not consider in this thesis as we focus on evolution and coalescence of single islands, rather than ensembles.

[43] revealed that the time τ_{eq} required for solid bodies to equilibrate towards their lowest-energy configuration is proportional to the fourth power of their length scale R , as

$$\tau_{eq} \propto R^4, \quad (2.7)$$

and, later on, Nichols and Mullins [46] and Brailsford and Gjostein [44] showed that, for coalescing spheres, the proportionality constant in Eq. (2.7) is

$$B = \frac{D_S \gamma \Omega^2 \rho}{k_B T}, \quad (2.8)$$

where D_S is the self diffusion coefficient, γ the surface energy, Ω the atomic volume and ρ the atomic density per unit area. Eq. (2.8) indicates clearly that, alongside deposition rate F , T is the main parameter that may be adjusted to influence the coalescence rate on growth experiments for a given material system. However, equilibrating solids must fulfill two fundamental conditions for Eq. (2.7) and Eq. (2.9) to be applicable. These equations are derived by calculating variations of the local chemical potential μ , which are the driving forces for atomic redistribution, with flux J given as

$$J = \frac{D_S \Omega \rho}{k_B T} \nabla \mu \quad (2.9)$$

μ in turn depends on the curvature K of the solid, as shown in the generalized Gibbs-Thomson equation

$$\mu \approx \mu_\infty + \Omega \left[\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta_1^2} \right) K_1 + \left(\gamma + \frac{\partial^2 \gamma}{\partial \theta_2^2} \right) K_2 \right] \quad (2.10)$$

[79]. It follows that, in order to compute J and arrive to Eq. (2.8), μ must be defined over the entire surface of the solid (Eq. (2.10)), and this surface must have a certain curvature K . Thus, this framework cannot account for solids either too small or exhibiting flat surfaces or facets, as the curvature cannot be obtained, or becomes a singularity, respectively. The latter case is of great relevance for many deposition experiments, since below a certain temperature T_R characteristic of each material—*roughening transition temperature* [63,81]—smooth facets start appearing on the

surfaces and coalescence dynamics cannot be predicted by means of near-to-equilibrium thermodynamic arguments. The absence of kinks on the facets implies that shape evolution cannot be derived by assuming a continuous system where atoms can detach, diffuse, and re-attach from- and to any point of the surface, as they only can become stable if they find another diffusing atoms in the facets and nucleate a new layer [81,82,83], and thus any treatment of coalescence under such conditions must include the kinetics of nucleation. In addition, all models available in the literature [38,39,48,49,76-78] approach the problem exclusively during annealing conditions, i.e., the fact that in deposition experiments condensation of the vapor phase brings extra mobile atoms to the surface of the nanostructures is not taken into account. For this reason, in Paper 3, by means of stochastic simulations and analytical modelling based on the thermodynamic arguments presented in Section 2.2, we attempt to understand the morphological evolution and dynamics during coalescence of 3D faceted islands, and the way by which this is affected by a deposition flux.

3 Kinetic Monte Carlo simulations

3.1 Atomistic model for island nucleation, growth and coalescence

In this work, we attempt to describe in an accurate way the morphological evolution and dynamics of islands grown on weakly-interacting substrates, mainly by means of stochastic simulations. Many available codes [38,48,77,78] used to simulate growth beyond submonolayer regime on weakly-interacting substrates rely on important simplifications such as the approximation of 3D islands to hemispheres. They are, thus, incapable of modelling island shape and morphology evolution, e.g., when the temperature falls below the roughening transition temperature and facets start forming. As we mentioned in previous chapter, these two growth stages play a main role in determining the final roughness and microstructure of films, and, for this reason, a fully atomistic kMC code is developed, which allows to study specifically these phenomena in a more accurate way.

3.2 The kMC method

The Kinetic Monte Carlo algorithm is at present a fundamental tool in the study of diverse physical systems in material science, due to both its efficiency compared with other methods, e.g., Molecular Dynamics [84], and its stochastic nature, which allows to perform statistically independent simulations of identical systems. Here, the kMC method is briefly reviewed in the context of film growth, while more details can be found in Refs. [85,86].

The aim of the kMC algorithm in this work is to simulate the deposition and growth dynamics of a thin film with a crystalline structure onto the surface of a solid substrate. In a real film/substrate system, all atoms vibrate around static lattice points due to thermal energy of the solid, and surface atoms have the possibility of escaping from local potential energy minima, or *sites*, and diffuse toward other sites. The diffusion of an atom over the surface can—excluding special processes as concerted motion [87] or exchange diffusion [88]—be thought as a chain of discrete jumps between neighbouring lattice sites, well separated by extensive periods in which the atom vibrates around its new position. During those time intervals, the entire film/substrate system remains in a metastable configuration, and thus it can be regarded to be in a

state i with average energy $\langle E_i \rangle$. This consideration implies that each individual atomic jump modifies the system configuration bringing it to a new and independent state j with average energy $\langle E_j \rangle$, and, by extension, that the surface evolves by a discrete series of transitions between states occurring randomly at mean rates⁷ $v^{i \rightarrow j}$. As all memory of previously visited configurations vanishes in the vibrations between consecutive transitions, the states are uncorrelated and the system is said to follow *Markovian dynamics*. This essential property is sufficient to define, in the framework of the theory of stochastic processes [89,90], the following set of master equations

$$\frac{dP(i,t)}{dt} = \sum_j \left(v^{j \rightarrow i} P(j,t) - v^{i \rightarrow j} P(i,t) \right), \quad (3.1)$$

which determine the way by which the probability $P(i,t)$ of finding the system in the state i at a given time t evolves. If there is knowledge that the system is certainly in i at t , $P(j,t) = 0$, and it will remain in i without transitioning during a time interval Δt , it is possible to integrate Eq. (3.1) over time to obtain

$$P(i, t + \Delta t) = \exp \left(- \int_t^{t+\Delta t} dt' \sum_j v^{j \rightarrow i} \right) = \exp(-K_{total}^i \Delta t), \quad (3.2)$$

where $K_{total}^i = \sum_j v^{j \rightarrow i}$. In this way, given any initial state i , there is a probability

$$P(i \rightarrow j) = \frac{v^{i \rightarrow j}}{K_{total}^i} \quad (3.3)$$

that a transition occurs to the state j in a time

$$\Delta t = - \frac{\ln(P(i,t+\Delta t))}{K_{total}^i}. \quad (3.4)$$

Note that Δt is not specifically dependent on the particular process $i \rightarrow j$, but on all possible processes.

⁷ When implementing the system computationally, the fact that atomic vibrations between diffusion jumps do not bring the system out of its current state i makes possible to neglect these vibrations, and define an unique spatial arrangement for this state with static atomic positions.

Figure 6. Flowchart of the kMC algorithm.

Initially, the kMC algorithm (i) sets time $t = 0$ (Fig. 6) and (ii) chooses an initial state i , which can be either a flat surface or an already-existing atomic configuration. In the next step (iii) it identifies N diffusion jumps between adjacent coordinated sites that may bring the system to a new state $j \in \{1, \dots, N\}$ and assigns a transition rate

$$v^{i \rightarrow j} = v_0 e^{\left(\frac{E_a^{i \rightarrow j}}{kT} \right)} \quad (3.5)$$

to each of them. In Eq. (3.5), $E_a^{i \rightarrow j}$ represents the energy barrier between i and j that must be overcome for the transition $i \rightarrow j$ to occur. If deposition is activated in the simulation, the arrival rate F of atoms to the surface is assumed constant and given as a simulation parameter. Then, the algorithm (iv) constructs a cumulative

set⁸ $\{K_1^i, \dots, K_j^i, \dots, K_N^i, K_{N+1}^i\}$ of elements $K_j^i = \sum_{k=1}^j v^{i \rightarrow k}$ associated with each process $i \rightarrow j$. By generating a random number $z_1 \in [0, K_{N+1}^i]$, it selects the process $i \rightarrow j'$ which fulfills the condition $K_{j'-1}^i < z_1 < K_{j'}^i$ (note that $K_n^i < K_m^i \forall n < m$) and (v) updates the system to the new state j' . In order to increase the simulation time t , (vi) it generates a second random number $z_2 \in (0, 1)$, equates it to the probability $P(i, t + \Delta t)$, and using Eq. (3.4) t is increased an amount

⁸ $K_{N+1}^i = \sum_{k=1}^N v^{i \rightarrow k} + F$

$$\Delta t = -\frac{\ln(z_2)}{K_{total}^i}. \quad (3.6)$$

Finally, the algorithm returns to step (iii) and iterates.

The method described above constitutes an unprecedented advance in the simulation of systems with atomic detail, but has a main drawback that may affect considerably its efficiency. Since the processes are chosen depending on their probability to occur, the fastest processes will always be more likely to happen. Thus, if the system is in a low-energy region of the configurational space from which is difficult to scape, but is connected to other energy states within this region, a kMC algorithm will simulate a large number of transitions between these states before it moves away from this low-energy region. This issue is called the superbasis problem. For certain types of systems, the portion of the overall computational time spent simulating transitions within the superbasis might be very large, so several solutions have been proposed, as documented in the literature [91,92].

In order to study metal thin film growth on weakly-interacting substrates, we develop an atomistic simulation code implementing the kMC algorithm. For the sake of computational efficiency, we force the atoms to occupy fixed positions on an hexagonal lattice with integer coordinates⁹ (on-lattice implementation), and calculate energy barriers using a bond counting scheme (see Section 3.3), which is validated against literature values [61,65,66,69] and nudged elastic band (NEB) calculations for Ag diffusion on Ag(111) (homoepitaxy).

⁹ It is also possible to assign the atoms to any point of the real space in the so-called off-lattice implementations [92,93,94], for more accurate, though costly, representations.

3.3 Bond counting scheme

The most fundamental part in the construction of a realistic kMC model is the creation of a complete and correct rate list, which entails the identification of the possible processes that may occur in the system in question, and the assignment of an appropriated occurrence rate to each of them, since the algorithm makes the system evolve based on a priori provided processes. Hence, failing to create this list, would inevitably lead to corrupted results. It is interesting to note that, given a correct process list, in case the rates are not correct but the hierarchy between their relative values remains approximately unchanged, time progression would not be calculated correctly but the macroscopic evolution of the system would remain intact in a qualitative sense.

In order to identify possible processes, for every atom with sufficient mobility (i.e., with a low enough coordination) for the system in state i , the algorithm scans its atomic environment and finds all neighboring sites to which it can diffuse. Previous knowledge of the system is convenient since relevant processes as interlayer [67-71] diffusion might not be identified by the algorithm and require a specific implementation for the model to reproduce a realistic version of the object of study. Once the possible atomic diffusion pathways $i \rightarrow j$ bringing the system to states j have been identified, a rate $\nu^{i \rightarrow j}$ is assigned to each of them by using Eq. (3.5), based on the energy barrier $E_a^{i \rightarrow j}$ that the atom needs to overcome in order to diffuse from the initial to the final sites. For the simplest models, these energies are obtained externally by experimental measurements [61,69] or theoretical calculations [65,66], and provided *a priori* to the simulations, so that the algorithm only needs to retrieve these values from a fixed list. This strategy is often limited to simple systems with a reduced number of possible processes, since this number grows drastically as the complexity of the system increases, and the process-identification becomes a colossal task. To solve this problem, using diverse computational techniques [84], energy barriers are calculated or constructed¹⁰ *ad hoc* as their corresponding processes are identified. If the new barriers are stored permanently in a growing list for subsequent retrieval, so that its

¹⁰ Note: to calculate a barrier implies to reproduce its associated process within a model implementing physical variables such as forces or electronic structure, whereas the barrier is constructed if a general and simple scheme applied for any process encountered is used.

calculation is performed only once, the algorithm is referred to as self-learning [92-98]. Many of these modern methods [91-94,97,98] are based in molecular dynamics or first principles calculations, approaches that, although highly accurate, require long times to compute the energy barriers as well as high computational power, and thus are able to simulate physical systems at restricted time scales.

As we are interested in modelling thin film growth beyond the nucleation stage, i.e., during relatively long timescales, we implement a *Bond Counting Scheme* (BCS) [99], a method in which the energy barriers are constructed as a function of the number of atomic neighbours at the initial and final positions of the corresponding diffusion jump. This operation allows for rapid barrier calculations, and, since it is of a purely arithmetic character, we are able to account not only nearest neighbour (NN) atomic interactions, but also next-nearest neighbour (NNN) and both fcc and hcp sites in our model, without compromising the efficiency of the simulations. The weakly-interacting substrate is implemented by lowering the pairwise adatom/substrate atom bond strength relative to the corresponding adatom/adatom value, thus resulting in a reduced energy barrier for adatom ascent onto the island second layer and sidewall facets. In our scheme, we construct the barrier $E_a^{i \rightarrow j}$ by an arithmetic sum of three elements,

$$E_a^{i \rightarrow j} = E_k^{i \rightarrow j} + \Delta E_b^{ij} + C_S, \quad (3.7)$$

where $E_k^{i \rightarrow j}$ is the kinetic barrier of the jump, ΔE_b^{ij} the potential energy difference between initial and final sites, and C_S a parameter which has a value when the diffusion jump is longer than usually, such an atom descending to a layer below by step crossing. For the sake of a clearer representation, $E_k^{i \rightarrow j}$ can be associated to the potential energy difference between the saddle point of the jump and the site, either initial or final, with higher potential energy, and C_S with the Ehrlich-Schwoebel barrier [67-71]. Additional details concerning the physical model and algorithm implementation are found in Paper 1.

3.4 Detailed balance and code validation

Regardless of the method employed for updating the rate list, when constructing a kMC model it must be ensured that the set of transitions between states of the system define a consistent energy landscape, in order for the master equations (Eq. (3.1)) to reproduce correctly the dynamics along the configurational space. This can be achieved by applying the *principle of detailed balance*, which states that, at equilibrium, each process should be equilibrated by its reverse process, expressed mathematically as

$$v^{i \rightarrow j} P(j, t) = v^{j \rightarrow i} P(i, t). \quad (3.8)$$

Letting our film/substrate system relaxate during a sufficiently long time to reach equilibrium, we can define a partition function

$$Z = \sum_i e^{-\frac{E_i}{kT}} \quad (3.9)$$

which accounts for all the accesible states of the system, and allows to derive the probabilities

$$P(i, t) = \frac{e^{-\frac{E_i}{kT}}}{Z}. \quad (3.10)$$

Hence, by inserting Eq. (3.5) and Eq. (3.10) into Eq. (3.8), we obtain

$$E_i - E_j = E_a^{i \rightarrow j} - E_a^{j \rightarrow i}. \quad (3.11)$$

The important feature of Eq. (3.11) is that all its constituent terms are fixed values which remain unchanged even if the system is not in equilibrium—note that Eq. (3.11) does not imply Eq. (3.8) if we cannot define a partition function (Eq. (3.9))—and therefore to impose this condition when calculating energy barriers suffices to not only fulfill detailed balance, but also for ensuring a consistent energy landscape. Since the energies E_i and E_j are constant values, if the equality did not hold, the energy value of the saddle point would be dependent of the direction in which it is crossed.

For kMC codes implementing simple methods for obtaining energy barriers on film/substrate systems, e.g. a bond counting scheme based on nearest neighbours

interactions on a cubic lattice [100], to track the processes and their reverse counterparts in order to ensure that detailed balance is fulfilled is a straight-forward task, whereas verifying this principle at more elaborated representations becomes easily unfeasible. Good examples of such representations are off-lattice implementations [92,93,94], multiple atom species on the film and substrate [101,102], and more detailed descriptions of the local environment of each atom [96]. The consequence of the inherent complexity of the previous representations is that detailed balance cannot be rigorously ensured, and can be only assumed to be virtually correct if simulation results are consistent with established knowledge. For instance, the physical correctness of our bond counting scheme is validated by replicating characteristic homoepitaxial growth modes for single islands, shape evolution of 3D islands upon annealing (Paper 1) and coalescence scaling laws (Paper 3).

4 Mathematical modelling of island dynamics

4.1 Top-layer nucleation

Besides stochastic simulations, we choose to study the problem of 3D island shape evolution by an approach based on elementary mathematical modelling. Growth of 2D islands with several layers in homoepitaxy conditions has been previously investigated in this manner through the concept of critical radius R_c [67,68,103], defined as the average radius of the top layer of an island which is required for the nucleation of a new layer to take place. These models are, however, only applicable to the common case of islands in homoepitaxial substrates bounded by Ehrlich-Schwoebel barriers, where the interlayer diffusion is constrained to only one direction and nucleation depends on atoms deposited directly on the island top (Fig. 7.a); the energy barrier for step crossing from the island edge to the top layer is prohibitively large, and virtually no atoms undergo this process. For the case of 3D islands on weakly-interacting substrates the situation is qualitatively different, as the weak bonding between substrate and deposit atoms results in a lower barrier for upward diffusion which leads to an ascending mass flux (Fig. 7.b) that is not accounted in state-of-the-art models. In addition, the edges of the layers above may expand and reach the edges of the layers below, forming low-index facets which facilitate even further the transport of mobile atoms from the island bottom to its top (See Section 2.3). Our goal is thus to expand existing models by including the upward mass flux and

Figure 7. Possible pathways for adatom arrival from the vapor phase to the top layer of an island growing on a) a homoepitaxial substrate and b) a weakly-interacting substrate.

investigate how the latter influences the island growth dynamics predicted for homoepitaxial systems. For this purpose, in Paper 2 we approach the problem by calculating the density of mobile atoms on and around a single 3D island, via diffusion equations, and then combining it with the probabilistic model developed by Krug *et. al.* [68], which allows to capture the general trends of the system with a simple analytical description (note that the aim is not to develop an accurate modelling tool to compute quantitative predictions).

4.2 Atomic densities by diffusion equations

For a surface with diffusing atoms, we can relate the local atomic density $u(\vec{r}, t)$ as a function of position and time, and the rate σ of generation of atoms per unit surface and unit time¹¹, with the mass flux $\vec{j}(\vec{r}, t)$ through the well-known continuity equation in its differential form

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{j} = \sigma. \quad (4.1)$$

In order to exclude explicitly the term $\vec{j}$ from our model, we can trivially combine Eq. (4.1) with Fick's first law of diffusion

$$\vec{j} = -D(u, \vec{r}) \nabla u(\vec{r}, t), \quad (4.2)$$

where the diffusivity $D(u, \vec{r})$ is a proportionality constant between $\vec{j}$ and the gradient of the atomic concentration $\nabla u(\vec{r}, t)$, to obtain the general *diffusion equation*

$$\frac{\partial u(\vec{r}, t)}{\partial t} = \nabla \cdot [D(u, \vec{r}) \nabla u(\vec{r}, t)] + \sigma. \quad (4.3)$$

This partial differential equation describes the collective behavior of the atoms in the surface resulting from the random movement of each atom, and once solved it returns the local density of mobile atoms $u(\vec{r}, t)$. Assuming an homogeneous surface without defects, i.e., with constant diffusivity, we can write Eq. (4.3) as

¹¹ Positive generation is referred as a source (e.g., deposition from vapor-phase) while negative generation is referred as a sink (e.g., surface desorption). σ is thus written as a sum of source and sink terms.

Figure 8. Faceted 3D island obtained from kMC simulations, generated with the visualization freeware Ovito [104].

$$\frac{\partial u(\vec{r}, t)}{\partial t} = D \nabla^2 u(\vec{r}, t) + \sigma, \quad (4.4)$$

which corresponds to Fick's second law of diffusion and is mathematically analogous to the heat equation. Our goal is to develop a simple analytical model of the island dynamics, and this leaves a rigorous representation of its non-trivial facet structure (Fig.8) out of our scope. For this reason, we approximate the 3D island to a cylinder with an unique smooth facet (Fig. 9), with equivalent areas on the top and the sidewalls, where atoms deposited on the substrate attach

isotropically. This approximated geometry has polar symmetry around the revolution axis of the cylinder and thus allows to further simplify Eq. (4.4) to a single spatial dimension,

$$\frac{\partial u(x, t)}{\partial t} = D \frac{\partial^2 u(x, t)}{\partial x^2} + \sigma. \quad (4.5)$$

The use of this diffusion equation enforces three further approximations into the model. First, that the surface is modelled as a continuous medium and the only information available of the surface is an averaged diffusion coefficient where the adsorption site structure and energetics are implicit. Second, that the adatom density is sufficiently low that adatom-adatom interactions can be neglected, as Eq. (4.5) only accounts for material densities, sources and sinks, and including interaction information in these terms could become a difficult task. Third, that the density of diffusing atoms is associated to a continuous variable u . Evidently, assigning a real number to a discrete quantity as the number of atoms implies that the results must be understood in probabilistic terms, i.e., measuring $u(r, t)$ in an ensemble of identically prepared systems will yield an average atom density $\langle u(r, t) \rangle$. However, in order to simplify Eq. (4.5) to a degree that allows for calculating analytical solutions, we need to address the aspect of how the time variable is treated, which we do in next section.

Figure 9. Mathematical representation of a 3D island with an area πR^2 on its top and a total area $2\pi R h$ on its sidewall. Here, F is the deposition flux, A' the capture area, γ the trapping parameter and u_t and u_f the atom densities on the top and the facet, respectively.

4.3 Steady-state approximation

Partial differential equations require, in most cases, to be solved numerically. In particular, in order to solve equations describing temporal evolution of physical quantities such as radiation, waves, probability functions or diffusion (Eq. 4.3), space and time are discretized and system evolution is computed iteratively. All techniques implementing this general strategy are called finite difference methods [105]. However, although highly effective in providing accurate numerical solutions, they do not constitute an optimal research tool for analyzing qualitative trends, and for this reason, we choose to make an extra assumption for simplifying the diffusion model and being able to solve it analytically.

We make the *steady-state approximation*: since the time scales between atomic motion and macroscopic changes on island morphologies differ by various orders of magnitude, it is fair to assume that the adatom population of the substrate/island system reaches an equilibrium configuration after each small change in the island shape, remaining constant at time intervals. In this way, considering a certain point of

the growth of the island, the time dependence vanishes and we can calculate the atomic densities for island top and facets easily from the simple differential equations

$$\frac{D_{top}}{r} \frac{d}{dr} \left(r \frac{du_{top}(r)}{dr} \right) + \sigma_{top} = 0 \quad (\text{top}) \quad (4.6a)$$

$$D_{facet} \frac{\partial^2 u_{facet}(z)}{\partial z^2} + \sigma_{facet} = 0 \quad (\text{facet}) \quad (4.6b)$$

r and z are the radial and vertical coordinates in the cylindrical coordinate system. By suppressing the time dependence, we are restricted to model only the stage of growth in which the shape of the island remains constant over time. That is, if we extract information about nucleation probability from densities calculated with this model for islands with different sizes, then islands must also have the same shape, since any change in their morphology will not be accounted in Eq. (4.6). From previous studies (see Paper 1) we know that, once islands have reached a certain size, they keep growing in a self-similar manner maintaining their characteristic facet structure, which allows us to apply the steady-state approximation at this growth stage.

To assume a constant adatom density requires a further consideration, related with the generation σ of atoms: the latter must evidently been time-independent. This implies that the rate of adatoms arriving to the system is constant and equals the rate of adatoms leaving the system, because in other case the difference in the incoming and outcoming fluxes would result in adatom accumulation and in turn density fluctuations over time. The adatom sources and sinks are deposition and attachment to the island facets, respectively, and we neglect desorption from the substrate. Atoms on the island will attach to the growing facets at the same rate they arrive, but still they must arrive at a constant rate, which only occurs if the island density on the substrate has saturated to a constant value. In this situation, the capture area of the island¹² does not change over time and all the atoms deposited in this part of the substrate will diffuse to the island, thus maintaining a constant arrival rate. If a new nucleation event would take

¹² The capture area [106,107] of an island refers to the region of the substrate for which deposited atoms will migrate towards that island, instead to any other.

place close to an island, the capture area of the latter would automatically be reduced, with the subsequent change on its incoming adatom flux.

4.4 Microscopic processes

Since our goal is to study how an upward mass transport influences the top-layer nucleation probability, we need to include in the model the microscopic processes associated with this transport. These processes are detachment from the substrate toward the island facets, attachment to growing layers and kinks on the facets, and crossing between the facets and the top layer. Including adatom ascent from the substrate to the island is straightforward, as a consequence of the steady-state and low-adatom-density conditions: each adatom diffuses upward from the island bottom before the next adatom arrives, since otherwise they would probably meet and start a nucleating cluster where new incoming adatoms would be trapped, which violates both of the assumptions previously imposed. Thus, the adatom flux from the island bottom to the facets equals the deposition flux over the entire capture area. Attachment to growing layers on the facets is fairly more troublesome to include. The edge of a growing layer is a dynamic morphological feature of the system, whose size and spatial distribution change each time a new adatom attaches, and attempting to account for it would imply a detailed microscopic description, which collides with our objective of simplicity. To circumvent this problem we define a parameter γ that represents qualitatively the roughness of the facets, and by extension, the probability that adatoms diffusing on them find a highly-coordinated position. The goal of γ is therefore enabling to estimate how different morphologies of the facets affects the nucleation probabilities on the top, as the density of ‘trapping’ sites controls the upward mass flow from the substrate and the island growth rate. The last feature that regulates the adatom current is the intersection between the facets and the top layer, as the energy barrier for crossing between them, $E_a^{facet-top} = 0.31 \text{ eV}$, is considerably larger than that of terrace diffusion, $E_a^{terrace-terrace} = 0.08 \text{ eV}$ (Paper 1). We include this temperature-dependent process in our model through the boundary conditions of Eq. (4.6), which is possible because $E_a^{facet-top}$ is confined only in the facet-top boundary, and is not present all over a surface as the kinks on the facets. The final form of the

equations is shown in Paper 2, together with a more detailed explanation and further mathematical details concerning the construction of the model.

Finally, we apply the diffusion equations together with the appropriate boundary conditions, and once we obtain the atomic densities we calculate R_c by equaling the rate of top/layer nucleation to the rate of formation of a new complete facet. This simple formalism suffices for identifying growth trends for islands on weakly-interacting substrates, and these predictions are in agreement with experimental observations of both homo- and heteroepitaxy, as discussed in Paper 2.

5 SUMMARY OF PAPERS

Paper 1 studies the formation and morphological evolution of 3D metal islands grown on weakly-interacting substrates. For this purpose, a full atomistic kMC code is developed, which is validated by reproducing island morphological transitions and anisotropies characteristic of the Ag/Ag(111) film/substrate system and shape evolution of 3D islands upon annealing. Simulations reveal that, for metal islands on weakly-interacting substrates, above a certain temperature a sharp transition between 2D and 3D shapes takes place. The 3D islands are strongly faceted, and grow in a self-similar way, which is found by tracking the evolution of the height-to-radius aspect ratio of the islands. In addition, the chain of atomistic mechanisms leading to 3D growth, is identified from careful visualization inspections: 3D nuclei are first formed due to facile adatom ascent at single-layer island steps, followed by the formation of sidewall facets bounding 3D islands, which in turn facilitates upward diffusion from the base to the summit of the island. Lastly, we also find that the limiting atomic process which determines the final island height is the temperature-dependent rate at which adatoms cross from the sidewall facet to the island summit

Paper 2 extends the knowledge gathered in Paper 1 by studying the dynamics of 3D islands, through the concept of critical radius R_c . The kMC code is adapted to measure this quantity from the simulations, and it is found that it decreases when temperature increases. To support this result, an analytical framework based on diffusion equations and probabilistic considerations is developed to model the changes of R_c due to island morphology. This model agrees qualitatively with the simulations, and shows that for homoepitaxial film/substrate systems, the R_c increases with increasing temperature, which is consistent with experimental data on island growth, both in homoepitaxial and weakly-interacting substrates.

Paper 3 studies the growth stage following island growth, coalescence, focusing on morphological evolution as well as on the dynamics, and on the effect that deposition have on them. kMC simulations show that above the roughening transition temperature T_R , coalescence proceeds by isotropic surface diffusion, and the scaling exponent α between island radius and coalescence time matches the results of classical theories

5 SUMMARY OF PAPERS

of equilibration, which predict a value of 4. However, below T_R , where islands are faceted, coalescence proceeds by island absorption, and depends by 2D nucleation on island facets. α is also found to be different, taking values well-above 4. We repeat the simulations at low temperatures adding a deposition flux, which is found to accelerate the coalescence processs, and bring α closer to 4, without modifying the morphological evolution. A thermodynamic model based on the kinetic theory of nucleation is developed to assess the validity of the simulation results. This model shows good quantitative agreement with the simulations, confirming the observations, and also reveals that the effect of deposition is to explicitly lower the thermodynamic barrier for facet nucleation.

6 Future outlook

There are multiple ways in which this research could be continued. The most straightforward ones, regarding the technical side, would be to use the current code to gain deeper understanding of film growth dynamics by looking at different kinds of interactions between nanostructures, such as Ostwald ripening or coalescence of islands with different sizes, and to investigate growth for other substrate morphologies. These research projects would have the advantage of not needing any modification of the kMC simulation code in its current state, which would simply require a new parametrization of the Bond Counting Scheme for modelling other material systems with similar physical behavior.

Another direction could be to improve the quantitative accuracy of the simulations, by coupling the kMC code with deterministic modelling tools as Molecular Dynamics or Density Functional Theory, to merge the efficiency of the kMC algorithm for simulating extended time scales with the reliability of barrier calculations based on physical principles. This would enable realistic modelling of, for instance, binary metal alloy film growth, for which basic barrier construction methods prove to be rather oversimplistic, besides cumbersome, tasks. A code capable of modelling two interacting species over a foreign substrate would open new and interesting pathways to study film growth and its manipulation, as a plethora of additional micro- and macroscopic phenomena, such as controlled nucleation and material segregation, respectively, would come into play. In addition, it could be used to move further to the design of multicomponent nanostructures, in which each atomic specie requires specific spatial arrangements.

Lastly, several computational strategies could be implemented in order to realize one of the tasks for which the code was originally conceived, namely to simulate and characterize a complete film growth experiment from nucleation to continuous film formation from an atomistic point of view. The main candidate, in my opinion, would be to resolve the superbasin problem (see Section 3.2), which would accelerate significantly the simulation times, allowing to confirm with a robust approach all the

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results available describing late stages of film growth obtained by approximated methods.

7 APPENDIX

7.1 Parallel kMC

As mentioned in Section 3.1, one of the purposes of writing a fully atomistic code is to open the possibility of modelling film growth beyond the island coalescence stage, up to a continuous film. This task does not require any further development of the physical model, but has a fundamental issue concerning computational capabilities; in order to study collective phenomena such as elongation and percolation transition, it is necessary to simulate a surface able to host a large number of islands. Since the kMC algorithm is of serial nature, all the processes occurring in this vast surface from the deposition of the first atom until the completion of a continuous film would have to be evaluated one-by-one, which would require extremely long simulation times, leaving a conventional approach unfeasible.

Besides using strategies that accelerate the serial algorithm [86,87], there exists the possibility of exploiting the parallel architecture of modern supercomputers in order to perform simultaneously several tasks of a common simulation, using different interconnected computer processing units (CPU). For this work, we upgrade our code to a parallel version following the method devised by Y. Shim and J.G. Amar. [108] In the following lines we provide a concise description of the functioning of the new code. A more complete explanation about parallel kMC algorithms can be found in Ref. [109].

The main idea consist on, at the beginning of the simulation, dividing the substrate surface (global) into N adjoining stripes (local) (Fig. 11), and assign each of them to a CPU that will apply the serial kMC algorithm to make them evolve. After each of the CPU have simulated a certain time t_{synch} of its correspondent local surface, it stops and remains halted until all the others have stopped too, and then sends and receives information of the processes that took place in the boundaries to its neighbouring CPUs, so that all the local surfaces together constitute a global evolving surface. This step is called synchronization, and t_{synch} , synchronization time, which is the inverse of the rate v_{fast} of the fastest process identified in the global surface,

$$t_{synch} = \frac{1}{v_{fast}} \quad (7.1)$$

Figure 10. Schematic visualization of the parallelization strategy, in which the global surface is decomposed in several local surfaces, each of them associated to an independent CPU.

The time t_o spent by the CPUs transferring information is called overhead time, and it depends on the volume of data transferred.

The main drawback of this implementation is that, once an atom diffuses through the boundary to another lattice, it remains immobile until its new position is sent to the corresponding boundary at the next synchronization. Although this effect is strictly unphysical, if the time the atom is inactive is kept under certain threshold it does not corrupt the evolution of the system. Contrarily, many inactive atoms may lead to undesired corrupted results, such as preferred island nucleation along the boundaries (Fig. 11).

We implemented the parallel algorithm successfully, but this particular strategy turned out to be incompatible with our purpose and the project remains currently on hold.

Figure 11. Snapshot of a parallel film growth simulation, in which long synchronization times between CPU corrupt a realistic physical system evolution, by causing preferential nucleation at the boundaries between surfaces. These boundaries can be localized from the parallel diagonal lines formed by rows of islands, marked with dashed lines.

The main issue arised from the wide range of timescales in the simulation process list; the presence of very fast diffusion processes—in general between hcp and fcc sites—requires short synchronization times (Eq. (7.1)), which implies that the number of synchronizations n necessary for evolving the film/substrate system a certain time t_{sim} is very high compared with more simple surface descriptions. In this way, the total time t_{total} spent by the machines (the time we have to wait for the results) to simulate t_{sim} ,

$$t_{total}(t_{sim}) = t_{sim} + n(t_{synch})t_0, \quad (7.2)$$

increases considerably. In our implementation, the efficiency gain attained with the parallel computing algorithm is overshadowed by the lost due to very frequent synchronizations.

A possible solution would be to remove the hcp sites from the surface model, which would reduce considerably $n(t_{synch})$: on a homoepitaxial substrate, at 300 K, the jump frequency of an Ag atom from an hcp to a fcc site is 20 times larger than the frequency between two fcc sites, and it follows that by supressing the former process only one out of twenty synchronizations for simulating t_{sim} . However, the strong

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feature of our code is precisely the implementation of hcp sites, from which the morphology asymmetries in nanostructures origin (e.g., truncated triangular shapes of islands grown in homoepitaxial substrates [61]). Without them, only a crude reproduction of the film growth process is possible, so we are still looking for a solution or an alternative strategy for approaching this research project.

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