Understanding the growth of nanocluster films

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Abstract

What are the mechanisms leading to the growth of nanostructures when preformed clusters are deposited on a surface? We present here the main physical processes which control the density and shape of the islands. As these processes span a large time scale, their understanding demands a variety of simulation approaches. We will focus here on an important issue for future technological applications of cluster deposition: the relation between the size of the incident clusters and the size of the islands obtained on the substrate. Kinetic Monte Carlo simulations of two- and three-dimensional islands show that the shape relaxation of the nanocrystallites cannot be explained by the usual theories of equilibration. Indeed, below the roughening temperature, the relaxation is much slower, kinetics being governed by the nucleation of a critical germon on a facet. This dramatically changes the size dependence of the equilibration time. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Growth of new materials with tailored properties is one of the most active research directions for physicists, the electronics revolution representing a paradigm. The search for smaller and smaller opto-electronic devices has lead to the new field of nanostructure growth, where one tries to obtain ordered arrays of structures containing a few atoms. There are different ways to build up nanostructured systems, the most popular being atomic deposition. Roughly speaking, the atoms deposited on the substrate diffuse and aggregate into islands of varying sizes. One would like to control the atomic diffusion and aggregation in order to form only the desired structures, adjusted in size, interparticle distance and, for alloys, atomic composition. This is a very difficult task, which has only been carried out in specific cases, mostly by taking advantage of elastic long range forces [1] or by “engineering” the substrate, i.e. by creating defects (as atomic steps) which act as nucleation centers [1,2].

Here we will focus on an alternative technique to form nanoislands on substrates, which consists in preforming the islands (as free clusters) before deposition and then depositing them. It should be noted that the cluster structure can be extensively characterized prior to deposition by several in-flight techniques such as time-of-flight spectrometry, photo-ionization or fragmentation [3]. Moreover, the properties of these building blocks can be adjusted by changing their size, which also affects the growth mechanisms, and therefore the

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film morphology [4]. There are several additional interests for depositing clusters. First, these are grown in extreme nonequilibrium conditions, which allows one to obtain metastable structures or alloys. For example, PdPt alloy clusters—which are known to have interesting catalytic properties—can be prepared with a precise composition (corresponding to the composition of the target rod, see below) and variable size and then deposited on a surface [5]. This allows one to tune within a certain range the properties of the films by choosing the preparation conditions of the preformed clusters. It might also be anticipated that cluster nucleation is less sensitive to impurities than atomic nucleation. Atomic island growth can be dramatically affected by them, as exemplified by the celebrated case of the different morphologies of Pt islands grown on Pt(111) [6] which were actually the result of CO contamination at an incredibly low level: \(10^{-10}\) mbar [7]. Instead, clusters, being larger entities, might interact less specifically with the substrate and its impurities.

2. Models of particle deposition

We describe in this section simple models which allow one to understand the first stages of film growth by low energy cluster deposition. These models can also be useful for understanding the growth of islands from atomic beams in the submonolayer regime in simple cases, namely (almost) perfect substrates, irreversible aggregation, etc., and they have allowed workers to understand and quantify many aspects of the growth: for a review of analysis of atomic deposition with this kind of models, see [1,8]. Given an experimental system (substrate and cluster chemical nature), how can one predict the growth characteristics for a given set of parameters (substrate temperature, incoming flux of clusters, …)?

A first idea—the “brute-force” approach—would be to run a molecular dynamics (MD) simulation with ab initio potentials for the particular system one wants to study. It should be clear that such an approach is bound to fail since the calculation time is far too large for present-day computers. Even using empirical potentials (such as Lennard-Jones (LJ), embedded atom or tight-binding) will not do because there is an intrinsically large time scale in the growth problem: the mean time needed to fill a significant fraction of the substrate with the incident particles. An estimate of this time is fixed by \(t_{\text{ML}}\), the time needed to fill a monolayer: \(t_{\text{ML}} \approx 1/F\), where \(F\) is the particle flux expressed in monolayers per second (ML/s). Typically, the experimental values of the flux are lower than 1 ML/s, leading to \(t_{\text{ML}} \geq 1\) s. Therefore, there is a time span of about 13 decades between the typical vibration time (\(10^{-13}\) s, the lower time scale for the simulations) and \(t_{\text{ML}}\), rendering hopeless any “brute-force” approach.

There is a rigorous way [9] of circumventing this time span problem: the idea is to “coarsen” the description by defining elementary processes, an approach somewhat reminiscent of the usual (length, energy) renormalization of particle physics. One “sums up” all the short time processes (typically, atomic thermal vibrations) in effective parameters (transition rates) valid for a higher level (longer time) description. We will now briefly describe this rigorous approach and then proceed to show how it can be adapted to cluster deposition.

2.1. Choosing the elementary processes

Voter [9] showed that the interatomic potential for any system can be translated into a finite set of parameters, which then provides the exact dynamic evolution of the system. Recently, the same idea has been applied to LJ potentials (Schroeder et al., 1997) by using only two parameters. The point is that this coarse-grained, lattice–gas approach needs orders of magnitude less computer power than the MD dynamics described above. Unfortunately, this rigorous approach is not useful for cluster deposition, because the number of atomic degrees of freedom (configurations) is too high. Instead, one chooses—from physical intuition—a “reasonable” set of elementary processes, whose magnitudes are used as free parameters. This allows one to understand the role of each of these elementary processes during the growth and then to fit their value from experiments. These are the models which we will study in this paper, with precise examples of parameter fit.
2.2. Predicting the growth from the selected elementary processes

To be able to adjust the values of the elementary processes from experiments, one must first predict the growth from these processes. The oldest way is to write “rate-equations” which describe in a mean-field way the effect of these processes on the number of isolated particles moving on the substrate (called monomers) and islands of a given size. However, this analytical approach is mean-field in nature and cannot reproduce all the characteristics of the growth. Two known examples are island morphology and island size distribution [10].

The alternative approach to predict the growth is kinetic Monte Carlo (KMC) simulations. KMC simulations are an extension of the usual Monte Carlo algorithm and provide a rigorous way of calculating the dynamical evolution of a complicated system where a large but finite number of random processes occur at given rates. KMC simulations are useful when one chooses to deal with only the slowest degrees of freedom of a system, these variables being only weakly coupled to the fast ones, which act as a heat bath. The “coarsened” description of film growth (basically, diffusion) given above is a good example, but other applications of KMC simulations include interdiffusion in alloys, slow phase separations, pinning/depinning transitions in dislocation diffusion,... The principle of KMC simulations is straightforward: one uses a list of all the possible processes together with their respective rates \( v_{\text{pro}} \) and generates the time evolution of the system from these processes taking into account the random character of the evolution. For the simple models of film growth described below, systems containing up to \( 4000 \times 4000 \) lattice sites can be simulated in a reasonable time (a few hours), which limits the finite size effects usually observed in this kind of simulation.

A serious limitation of KMC approaches is that one has to assume a finite number of local environments (to obtain a finite number of parameters): this confines KMC approaches to regular lattices, thus preventing a rigorous consideration of elastic relaxation, stress effects,... everything that affects not only the number of first or second nearest neighbors but also their precise position. Indeed, considering the precise position as in MD simulations introduces a continuous variable and leads to an infinite number of possible configurations or processes. Stress effects can be introduced approximately in KMC simulations, for example by allowing a variation of the bonding energy of an atom to an island as a function of the island size (the stress depending on the size), but it is unclear how meaningful these approaches are.

2.3. Basic elementary processes for cluster growth

What is likely to occur when clusters are deposited on a surface? We will present here the elementary processes which will be used in cluster deposition models: deposition and diffusion of the clusters and their interaction on the surface (Figs. 1 and 2).

A simple physical rationale for choosing only a limited set of parameters is the following (see Fig. 3). For any given system, there will be a
“hierarchy” of time scales, and the relevant ones for a growth experiment are those much lower than $t_{ML} \approx 1/F$. The others are too slow to act and can be neglected.

The hierarchy of time scales (and therefore the relevant processes) depends of course on the precise system under study. It should be noted that for cluster deposition the situation is somewhat simpler than for atom deposition since many elementary processes are very slow. For example, diffusion of clusters on top of an already formed island is very low [11], cluster detachment from the islands is insignificant and edge diffusion is not an elementary process at all since the cluster cannot move as an entity over the island edge (as we will discuss in Section 3.2, the equivalent process is cluster–cluster coalescence by atomic motion). Let us now discuss in detail each of the elementary processes useful for cluster deposition.

The first ingredient of the growth, deposition, is quantified by the flux $F$, i.e. the number of clusters that are deposited on the surface per unit area and unit time. The flux is usually uniform in time, but in some experimental situations it can be pulsed, i.e. change from a constant value to 0 over a given period. Chopping the flux can affect the growth of the film significantly [12].

The second ingredient is the diffusion of the clusters which have reached the substrate. We assume that the diffusion is Brownian, i.e. the particle undergoes a random walk on the substrate. To quantify the diffusion, one can use both the usual diffusion coefficient $D$ or the diffusion time $s$, i.e. the time needed by a cluster to move by one diameter. These two quantities are connected by $D = d^2/(4\tau)$, where $d$ is the diameter of the cluster. Experiments show that the diffusion coefficient of a cluster can be surprisingly large, comparable to the atomic diffusion coefficients. The diffusion is here supposed to occur on a perfect substrate. Real surfaces always present some defects such as steps, vacancies or adsorbed chemical impurities. The presence of these defects on the surface could significantly alter the diffusion of the particles and therefore the growth of the film [8].

The last simple process we will consider is the interaction between the clusters. The simplest case is when aggregation is irreversible and particles simply remain juxtaposed upon contact. This occurs at low temperatures. At higher temperatures, cluster–cluster coalescence will be active (Fig. 2). Thermodynamics teaches us that coalescence should always happen but without specifying the kinetics. Since many clusters are deposited on the surface per unit time, kinetics is here crucial to determine the shape of the islands formed on the substrate. A total comprehension of the kinetics is still lacking, for reasons that we will discuss later (Section 3.2).

The usual game for theoreticians is to combine these elementary processes and predict the growth of the film. For example, in the simplest version of these models [8], where one only includes deposition, Brownian diffusion and irreversible aggregation, the saturation island density $N_{sat}$ (see Fig. 5a) obeys

$$N_{sat} = 0.41(F\tau)^{0.36}. \quad (1)$$
However, experimentalists are interested in the reverse strategy: from (a set of) experimental results, they wish to understand which elementary processes are actually present in their growth experiments and what the magnitudes of each of them are, what physicists call understanding a phenomenon. The problem, of course, is that with so many processes, many combinations will reproduce the same experiments (see specific examples in [8]). We will give a single example of how these models can help understand the physics of growth, and refer the interested reader to [8] for more details.

2.4. A simple case: $\text{Sb}_{2300}$ clusters on graphite HOPG

The growth of antimony cluster films has been thoroughly investigated [11] and represents a clear example of the interest of the Monte Carlo models. Fig. 4a shows a general view of the morphology of the antimony submonolayer film for $e = 0.14$ ML and $T_s = 353$ K. A detailed analysis [11] of this kind of micrographs shows that the ramified islands are formed by the juxtaposition of particles which have the same size distribution as the free clusters of the beam. From this, we can infer two important results. First, clusters do not fragment upon landing on the substrate. Second, antimony clusters remain juxtaposed upon contact and do not coalesce to form larger particles (Fig. 2a).

From a qualitative point of view, Fig. 4a also shows that the clusters are able to move on the surface. Indeed, since the free clusters are deposited at random positions on the substrate, it is clear that, in order to explain the aggregation of the clusters in those ramified islands, one has to admit that the clusters move on the surface. How can this motion be quantified? Can we admit that diffusion and pure juxtaposition are the only important physical phenomena at work here?

Fig. 5a shows the evolution of the island density as a function of the deposited thickness. We see that the saturation island density $N_{\text{sat}}$ is reached for $e \approx 0.15$ ML. This indicates [8] that evaporation or island diffusion are not important in this case. Therefore, we guess that the growth should be described by a simple combination of deposition, diffusion of the incident clusters and juxtaposition. This has been confirmed in several ways. We only give two different confirmations, directing the reader to [8] for further details. First, a comparison of the experimental morphology and that predicted by models including only deposition,
diffusion and pure juxtaposition shows a very good agreement (Fig. 4b). We have also shown [8] that the saturation island density accurately follows the prediction of the model when the flux is varied. If the islands were nucleated on defects of the surface, the density would not be significantly affected by the flux.

Having carefully checked that the experiments are well described by the simple DDA model, we can confidently use Eq. (1) to quantify the diffusion of the clusters. The result is a surprisingly high mobility of Sb, with diffusion coefficients of the same order of magnitude as the atomic ones, i.e. $10^{-9}$ cm$^2$ s$^{-1}$ (Fig. 5b). Moreover, the prefactor $D_0$ of the Arrhenius equation $D = D_0 \exp(-E_a/kT)$ is unexpectedly high: $D_0 = 10^4$ cm$^2$ s$^{-1}$. The canonical value for atomic diffusion is instead $D_0 = 10^{-3}$ cm$^2$ s$^{-1}$, seven orders of magnitude lower! We have no explanation of this huge difference at the moment, although it is interesting to note that Wang et al. [13] have also found high prefactors for cluster diffusion when the cluster moves by gliding as a whole on the surface.

3. How do clusters diffuse and coalesce?

In the preceding sections we have tried to analyze the film growth with the help of two main ingredients: diffusion of the clusters on the surface and their interaction. We have taken the diffusion as just one number quantifying the cluster motion, without worrying about the microscopic mechanisms which could explain it. For atomic diffusion, these mechanisms have been extensively studied and are relatively well known. In the (simplest) case of compact (111) flat surfaces, diffusion occurs by site-to-site jumps over bridge sites (the transition state). Therefore, diffusion is an activated process and plotting the diffusion constant vs. the temperature yields the height of the barrier, which gives information about the microscopies of diffusion. This kind of simple interpretation is not valid for cluster diffusion. It is always possible to infer an “activation” energy from an Arrhenius plot (see Fig. 5c) but the meaning of this energy is not clear since the precise microscopic diffusion mechanism is unknown. Similarly, cluster–cluster coalescence (Fig. 2) has been supposed to be total or null (i.e. pure juxtaposition) but without considering the kinetics or the intermediate cases which can arise.

In this section, we describe some simulations which can shed light on the microscopic mechanisms leading to cluster diffusion or coalescence.

3.1. 3D island diffusion mechanisms

It has been shown [8,14] that the main parameter determining the mobility of 3D islands on a
substrate is the possible epitaxy of the cluster on the substrate. Indeed, if the island reaches an epitaxial orientation, it is likely to have a mobility limited by the individual atomic movements, which give a small diffusion constant (of order $10^{-17}$ cm$^2$ s$^{-1}$ at room temperature). Diffusivities of this magnitude will not affect the growth of cluster films during typical deposition times, and clusters can be considered immobile. If the island is not in epitaxy on the substrate, high mobilities can be observed because the cluster sees a potential profile which is not very different from that seen by a single atom. It should be noted that this nonepitaxy can be obtained when the two lattice parameters (of the substrate and the island) are very different, or also when they are compatible if there is relative misorientation. MD simulations [14] show that, for LJ potentials, only homoepitaxy prevents clusters from moving rapidly on a surface. It should be noted that relaxation of the cluster or the substrate—which would favor a locking of the cluster in an energetically favorable position at the expense of some elastic energy—has not been observed in these LJ simulations. Another important parameter is the cluster–substrate interaction: one can think that a large attractive interaction (for metal on metal systems, for example) can induce an epitaxial orientation and prevent the cluster from diffusing, even in the heteroepitaxial case.

### 3.2. Cluster–cluster coalescence

What happens when two clusters meet? If they remain simply juxtaposed, morphologies similar to Fig. 4a are observed. In this case, the incident clusters have retained their original morphology, and the supported particles are identical to them, even if they are in contact with many others after cluster diffusion. It is clear, by looking for example at Fig. 6, that in some experimental situations the supported islands are clearly larger than the incident clusters, indicating that some coalescence has taken place. How can one understand and predict the size of the supported particles? Which are the relevant microscopic parameters? This is an interesting question from the fundamental point of view, since it is not clear that the theoretical tools which have been developed to deal with the kinetic evolution of macroscopic objects (size larger than a micrometer) by Herring [15] and Nichols and Mullins [16] can be used at the nanometer scale. These equations, which are based on coarse-grained, continuous equations, lead to an equilibrium time $t_{eq}$ which increases as the fourth power of the object linear size. For example, one could wonder whether sintering of ceramic or metallic nanopowders can be analyzed with these classic tools since it is not clear that macroscopic concepts such as curvature, chemical potential, etc., should retain their relevance when dealing with structures containing only a few atoms. Studying the validity of the partial differential equations approach at various length scales and temperatures is important since this formalism is also used by experimentalists to interpret their data and by theoreticians as a black box to calculate the time evolution of different structures [8,17–20].

Several authors [21–23] have studied the kinetics of unsupported cluster–cluster coalescence by MD simulations. They have shown that the first stages (a few ns) of this process consist in a plastic deformation of the particles leading to the building of a “neck” at their contact point. Then, the evolution seems to stop at the time scales that can be reached by this kind of approach. This “locking” has been attributed [21] to the presence of facets.
The precise role of the facets in the coalescence process is a subject of current interest. Experiments have shown that shape evolution is very slow in presence of facets for 3D crystallites [24]. To investigate this point further, we have carried out extensive KMC simulations of 2D and 3D cluster–cluster coalescence. These simulations are not intrinsically limited in the time scales that can be investigated and could therefore help in understanding the role of facets and the limitations of the continuous approach.

3.2.1. Physical model

We use standard KMC simulations to study the equilibration of 2D (3D) crystallites having a triangular (fcc) crystalline structure. Since we are only interested in finding generic laws for the size dependence of $t_{eq}$ (which should not depend on the details of atom–atom interaction), we have chosen a very simple energy landscape for atomic motion [25]. We assume that the potential energy $E_p$ of an atom is proportional to its number $i$ of neighbors, and that the kinetic barrier $E_{act}$ for diffusion is also proportional to the number of initial neighbors, before the jump, regardless of the final number of neighbors, after the jump $E_{act} = -E_p = iE$, where $E$ sets the energy scale ($E = 0.1$ eV throughout the paper). Therefore, the probability $p_i$ per unit time that an atom with $i$ neighbors moves is $p_i = v_0 \exp[-iE/k_B T]$, where $v_0 = 10^{13}$ s$^{-1}$ is the Debye frequency. Thus, our simple kinetic model includes only one parameter, the ratio $E/k_B T$, where $k_B$ is the Boltzmann constant and $T$ the absolute temperature. The initial configuration of the clusters is elongated, and we stop the relaxation when the crystallites are close to equilibrium, with an aspect ratio of 1.2.

3.2.2. Simulation results

Figs. 7a and b show log–log plots of the relaxation time as a function of the linear dimension of the 2D and 3D islands, respectively. The comparison between two and three dimensions reveals, as happens with all comparisons, some similarities and some differences. In both cases, the continuous approach, which predicts a slope of 4, is correct only for the highest temperatures. The physics behind the failure of this macroscopic approach is also similar [25,26].

At high temperatures, the island perimeter (surface) is rough, full of traps for the diffusing atoms, and the usual (individual) atomic surface diffusion is efficient to transfer mass from the high chemical potential regions (the tips of the islands) to the low potential ones (the center of the island). Herring [15] and Nichols and Mullins [16] have quantified this physical process long ago: taking the chemical potential as proportional to the local curvature, and using matter conservation and linear response theory, one reaches inevitably the fourth power law in agreement with our Monte Carlo simulations. This result then validates the use of the concept of curvature at microscopic scales.
At lower temperatures, facets begin to appear, and single atom diffusion can no longer transfer matter from the tips to the center, because these atoms simply wander on top of the facets to become trapped again in the tips. Therefore, a supplementary step has to be overcome for the island to approach equilibrium: the nucleation of new atomic lines or terraces. So far, flat and 3D islands behave similarly: now come the differences, since, after all, when the temperature is lowered, the size-dependence exponent rapidly increases in three dimensions, whereas it slowly decreases in two dimensions (Figs. 7a and b).

In three dimensions, the increase of the size exponent (which is actually due to an exponential behavior) is a consequence of the presence of a nucleation energy barrier which depends on the crystallite size [26]. The nucleation of a germ on a facet is formally similar to the creation of a liquid germ within a gas phase, except that in our case the chemical potential of the atoms in the “gas” depends on the size of the crystallite because these atoms come from the tips, whose curvature (which fixes the chemical potential, see above) is size dependent. Therefore, as the crystallite size increases, an ever larger nucleation barrier has to be overcome, which induces an exponential increase in the relaxation time. In two dimensions, a careful analysis [25] shows that the decrease of the exponent leads to an N dependence of the relaxation time at very low temperatures. Due to the presence of facets, the diffusion is not at all a limiting process, and the limiting step of the relaxation is the nucleation of a germ of the size of the smallest facet on a larger facet [27]. The average time \( \tau_2 \) needed to create a two-particles germ on a facet can be shown to be independent of the size of the facet: \( \tau_2 \propto \tau_i^2/\tau_2 \) (where \( \tau_i = 1/p_i, p_i \) defined in Section 3.2.1). This step is the most difficult one of the creation of the critical germ: it imposes its activation energy on the limiting step duration. Once a two-particles germ has been created, the germ has a probability \( 1/(l-2) \) to grow up to the critical size \( l \) without disappearing [27]. The duration of the whole limiting step of the relaxation is then about \( \tau_\text{limiting} \propto \tau_i^2(l-2)/\tau_2 \propto \tau_i^2/N/\tau_2 \). It is important to note that \( \tau_\text{limiting} \) is the time to transport \( l/ \) particles from a facet to another. If \( L \) is the size of the largest facet, the nucleation of a critical germ has to be repeated about \( L - l \) times so that the crystallite goes back to its equilibrium shape. The relaxation time then scales as: \( \tau_\text{relaxation} \propto (L - l)\tau_i^2/l/\tau_2 \propto \tau_i^2N/\tau_2 \).

4. Conclusions

The combination of Monte Carlo and molecular dynamics simulation techniques can shed light on the physics of nanostructure growth from cluster beams. Specifically, by comparing the experimental evolution of the island density as a function of the number of deposited particles to the predictions of computer simulations, one can obtain quantitative information about the relevant elementary processes. For example, we have shown that large clusters can move rapidly on the surface, with diffusion constants comparable to the atomic ones. To understand this high diffusivity at the atomic level demands the use of MD simulations [14]. Concerning cluster–cluster coalescence, it has been suggested that this process can be much slower than predicted by the usual sintering theories, because of the cluster facets. Below the roughening transition, the route to equilibrium has to involve nucleation of new atomic planes, which needs more time, leading to an exponential increase of \( t_\text{eq} \) as a function of the cluster size for 3D crystallites.

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