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## A FRACTAL MODEL FOR THE FIRST STAGES OF THIN FILM GROWTH

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### Abstract

In this paper, we briefly review a model that describes the diffusion-controlled aggregation exhibited by particles as they are deposited on a surface. This model allows us to understand many experiments of thin film deposition. In the Sec. 1, we describe the model, which incorporates deposition, particle and cluster diffusion, and aggregation. In Sec. 2, we study the dynamical evolution of the model. Finally, we analyze the effects of small cluster mobility and show that the introduction of cluster diffusion dramatically affects the dynamics of film growth. Some of these effects can be tested experimentally.

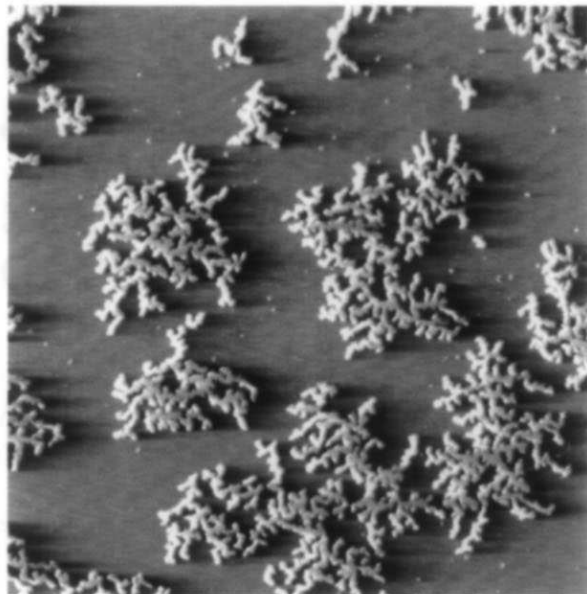
### 1. INTRODUCTION

Understanding the processes underlying the growth of thin films has led to widespread interest,<sup>1</sup> both from the theoretical<sup>1-8</sup> and the experimental points of view.<sup>9-12</sup> Recently,

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improvements in experimental techniques — such as scanning tunneling microscopy — permit the investigation of atomic details of the embryonic “sub-monolayer” stages of film growth. Recent experimental works<sup>10-12</sup> have shown that *fractal* structures can be formed during the first stages of the growth (Fig. 1). Then, it is interesting to try to analyze the growth in the framework of fractal models. One might consider the use of the percolation



(a)



(b)

**Fig. 1** Experimental images of the first stages of growth for films prepared by (a) Atomic deposition of Ag on Pd<sup>11</sup>; and (b) Deposition of Sb compact aggregates containing 2300 atoms on graphite.<sup>12</sup>

model<sup>13,14</sup> to describe certain experiments of surface deposition.<sup>15</sup> However, percolation assumes that particles do not diffuse after being deposited, when in fact not only diffusion but also aggregation of the diffusing particles takes place. There exist models of diffusing particles that aggregate, but such “Cluster-Cluster Aggregation” (CCA) models<sup>16</sup> do not allow the continual injection of new particles via deposition. Here, we develop a model that incorporates the three physical ingredients of thin film growth: Deposition, Diffusion and Aggregation (DDA). Similar models that neglect the shape of the islands or the possibility of cluster diffusion were studied independently.<sup>4,6</sup> We have shown in detail elsewhere<sup>5</sup> how the DDA model generates a wide variety of fractal structures characteristic of different models such as percolation, Diffusion Limited Aggregation (DLA)<sup>17,18</sup> or CCA. Here, we focus on the dynamics of film growth and the importance of (small) island diffusion.

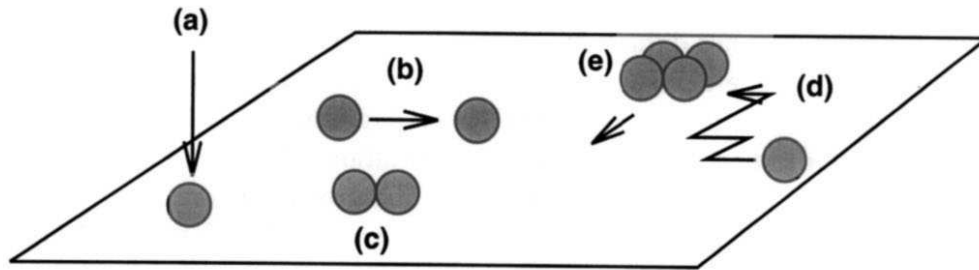
## 2. MODEL DESCRIPTION AND JUSTIFICATION

The DDA model is defined as follows (Fig. 2):

- (1) *Deposition.* Particles are deposited at randomly-chosen positions of the surface at a flux  $F$  per lattice site per unit time.
- (2) *Diffusion.* All particles and clusters (sets of connected particles) are chosen at random and attempted to move North, East, South or West by one lattice constant per unit time. The probability that they actually move is proportional to their mobility, which we assume to be given by  $D_s = D_1 s^{-\gamma}$ . Here  $s$  is the number of particles in the cluster,  $D_1$  is the diffusion coefficient for a monomer ( $s = 1$ ), and the parameter  $\gamma$  characterizes the dependence of  $D_s$  on cluster size.
- (3) *Aggregation.* If two particles come to occupy neighboring sites, they (and therefore the clusters to which they belong) stick irreversibly.

We call *particles* the isolated atoms (or monomers) that are deposited on the surface, *clusters* any set of connected particles (including the monomers) and *islands* the clusters containing more than one particle. Physically, two competing mechanisms are introduced in the model, each one with its own time scale: deposition and diffusion. It is useful to introduce the normalized flux defined as the number of particles deposited per unit site per *diffusion time*  $\tau$ , where  $\tau$  is the mean time needed by a monomer to jump by a lattice site. The monomer diffusion coefficient is then given by  $D_1 = 1/(4\tau)$ , and the normalized flux by  $\phi = F\tau$ . Then, from experimental values of  $F$  and  $D_1$ , it is possible to calculate  $\phi$  and the morphologies predicted by our model. The program actually calculates a probability for dropping a particle:  $p_{drop} = \phi L^2 / (\phi L^2 + N_{cl})$ , where  $L$  is the system size and  $N_{cl}$  is the total number of clusters present in the system. A random number  $p$  is chosen and compared with  $p_{drop}$ . If  $p < p_{drop}$ , a particle is added at a random position on the lattice. If  $p > p_{drop}$ , a cluster or a particle is chosen at random and attempted to move. In both cases, the time is increased by  $\tau / (\phi L^2 + N_{cl})$ .

It should be stressed that this is only a “zeroth-order” model which has the ambition to give a feeling on the relative influence of deposition and diffusion on the growth properties of films. Details specific to certain experimental systems, such as the existence of the Schwoebel barrier, the precise dependence of cluster diffusion on size, etc., are not carefully taken into account since we want to keep the DDA model as general as possible (see Ref. 5).



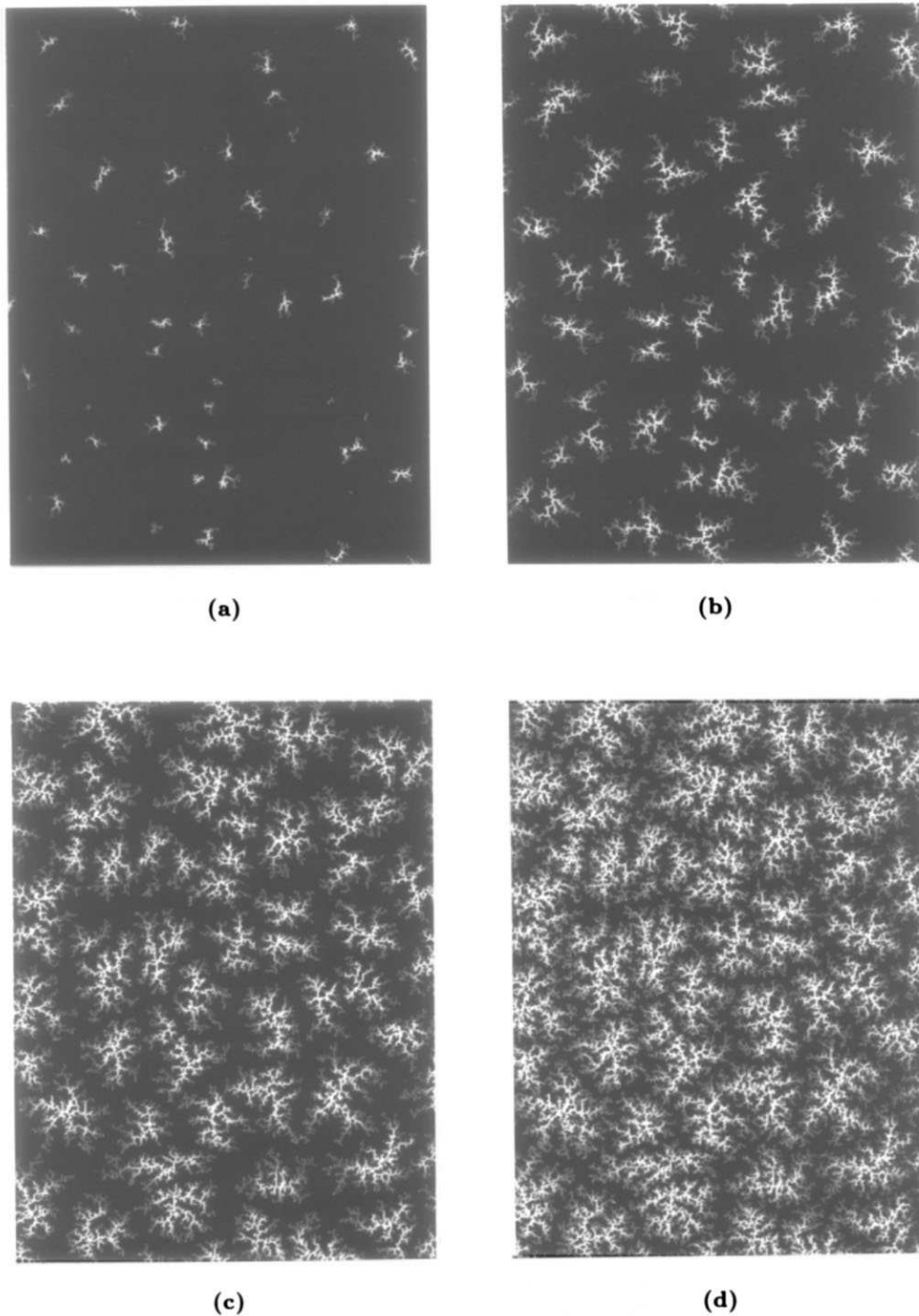
**Fig. 2** Schematic representation of the basic processes considered in this model: (a) deposition; (b) and (d) particle diffusion; (e) island diffusion; and (c) aggregation. (b) corresponds to *nucleation* (i.e., a new island (c) is created), while (d) corresponds to *growth* of an already existing island (see the text for details).

### 3. DYNAMICAL EVOLUTION

We present here snapshots of the system at different times to show the formation of the islands. These images were obtained for  $\phi = 1.2 \cdot 10^{-8}$  and  $\gamma = \infty$  (i.e., only monomers are allowed to move). A detailed presentation of the dynamical evolution of the model has been given elsewhere.<sup>5</sup> Actually, it is more interesting to use the surface coverage  $\theta$  instead of the time as the evolution parameter.  $\theta$  is defined as the ratio of the number of occupied sites to the total number of sites on the surface, and for the times studied here we have  $\theta \sim Ft$ .

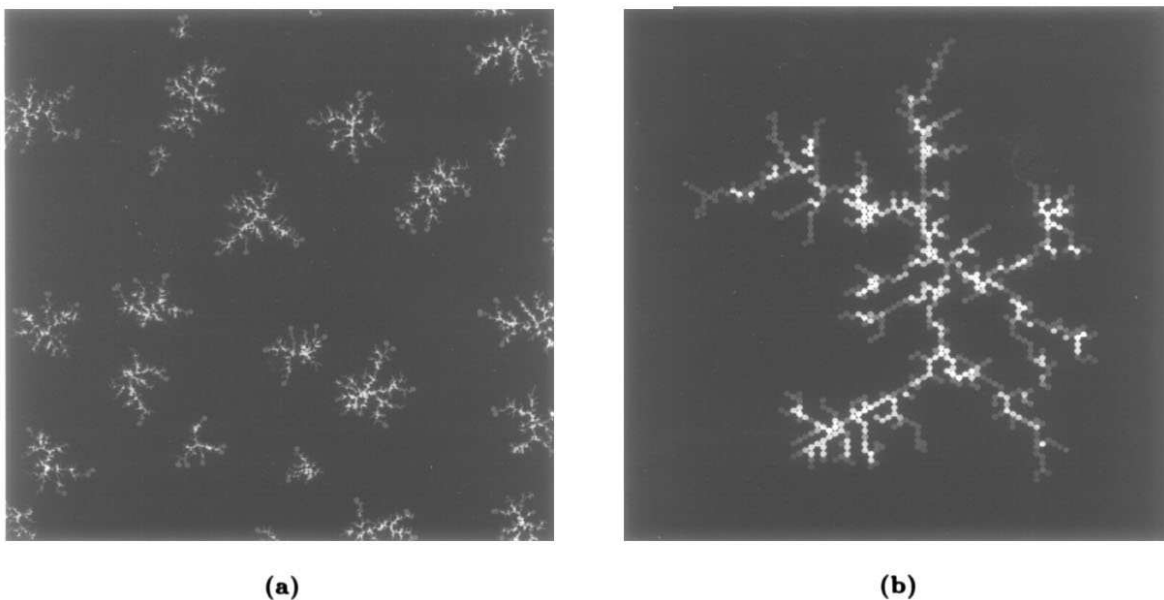
At very short times ( $\theta \leq 0.001$ ), mainly monomers (isolated particles) are found on the substrate, since they did not yet meet another one to form a cluster. Later, small clusters are homogeneously grown on the surface [Fig. 3(a)], and the island density (i.e., the number of islands per lattice site) starts to grow. These small clusters can be considered as the “nucleation centers” for the growth. As time increases, large clusters grow on these nucleation centers, by addition of single particles [Fig. 3(b)]. These clusters are very similar to those obtained experimentally [Figs. 1(a) and 1(b)]. We have found that their fractal dimension is 1.65, very close to the fractal dimension of the DLA clusters. This (DLA-like) growth mechanism goes on until the linear dimension of the clusters becomes comparable to the separation between them [Fig. 3(c)]. Then, many particles start to fall *inside* the clusters and their fractal dimension rapidly increases. Eventually, a cluster of a size comparable to the system size is built and the system spans [Fig. 3(d)]. At that time, the effective fractal dimension of the spanning cluster reaches a value close to 1.9.

It is interesting to note that the growth of the film for  $\gamma = \infty$  is in some loose sense “self-regulated” since islands tend to avoid each other, by growing preferentially in the directions where no island is present. The reason is that monomers are more abundant in those regions since no island captures them. Then, the probability for a given point of an island to grow is higher if it is far from other islands. This effect can be quantified in the following way. We first grow a system with a given coverage and we freeze the growth. Then, we deposit a monomer and we move it exactly as during the growth, but each time the monomer reaches an island, we record the point where it touched the island and *remove* it. By counting the number of monomers that hit each point, we can measure the growth probability within each island. Figure 4(a) shows a global view of these probabilities for a large system at a coverage of 0.04. The white points correspond to those point which grow slower and the bright blue points show the regions of high growth probability. Figure 4(b)



**Fig. 3** Morphologies obtained for a normalized flux  $\phi = 1.2 \cdot 10^{-8}$ , a system size  $L = 500$  and  $\gamma = \infty$ . The images show a portion  $290 \times 210$  of the lattice. Four different coverages (corresponding to four different times of deposition) are shown: (a) coverage 0.02; (b) coverage 0.1; (c) coverage 0.25; and (d) coverage 0.4. Colors indicate the order in which particles were deposited on the surface: the first particles deposited are colored white, then yellow, orange, red, blue and finally green.

shows in detail the growth probabilities for one of the islands. The fact that each island has its own “capture zone” and grows inside it, has some interesting consequences on the size distribution of the islands. This will be discussed below.



**Fig. 4** Growth probabilities for different points of the islands at a coverage 0.04 ( $\gamma = \infty$ ). (a) global view of the surface; (b) detailed view of an island. Colors give the probability that a given site of the island has to catch a monomer. The probability increases in the order: white, yellow, orange, red, blue, green and finally big bright blue dots.

#### 4. ISLAND DIFFUSION

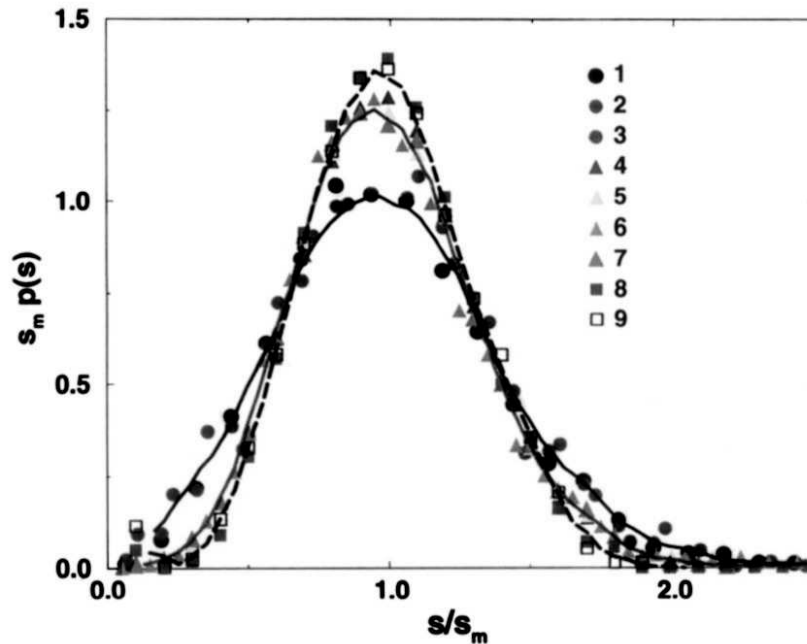
In the last paragraph, we have studied the behavior of the model in the case where only monomers are allowed to move. In this section, we want to address some consequences of (small) cluster diffusion. It has long been recognized that cluster diffusion can influence the growth of the films,<sup>2,19</sup> even if at that time experimental proofs were lacking. Recently, experiments<sup>20</sup> and molecular dynamics studies have shown that small clusters can move on the surfaces without breaking.<sup>21</sup> Generally, however, the experimental results are analyzed within the framework of the different models containing only monomer diffusion. These models can include *reversible* aggregation,<sup>8,22</sup> meaning that two monomers that aggregate can detach after a certain time. This can lead to wrong interpretations if small cluster mobility is indeed present in the experiments.<sup>23</sup> Then, it is important to understand the consequences of this mobility so as to be able to identify them in the experiments.

We have shown previously<sup>5</sup> that the introduction of cluster mobility considerably changes the growth dynamics of the film. Specifically, we have showed that:

- (1) The mean cluster size increases *exponentially* as a function of the coverage. A power-law dependence is generally found when only monomer diffusion is allowed. This effect is intriguing and may be due to large cluster diffusion.<sup>5</sup>
- (2) The maximum island density depends on the incident flux according to  $N_{\max} \sim F^{\zeta}$  with  $\zeta = 0.42$ , as opposed to  $\zeta = 0.33$  found with monomer diffusion. It is also known that when only *dimer* diffusion is introduced,  $\zeta = 0.4$ .<sup>7</sup> The problem is that generally the accuracy of the experimental determinations of  $N_{\max}$  is not high enough to distinguish between the different exponents.<sup>12</sup>
- (3) More interesting experimentally: the evolution of the island density as a function of coverage for low normalized fluxes (typically less than  $10^{-5}$ ). It is known<sup>4</sup> that the

maximum of the island density is reached only at roughly a coverage of 0.2, when only monomers can move. On the contrary, if clusters can move, this maximum is reached for *smaller* values of the coverage.

We add here a test that is easy to perform experimentally, and which has actually already been used to distinguish between different growth mechanisms<sup>12,23,24</sup>: the rescaling of island size distributions.<sup>8,25</sup> The idea is to rescale the island size distributions into a universal distribution that depends on the ingredients of the model (i.e., the detailed mechanisms of Deposition, Diffusion and Aggregation), but not on the values of the flux or the coverage. Very recently, Mulheran and Blackman<sup>26</sup> have given some interesting insights into why such a universal function should exist, at least for the case of heterogeneous growth. Their argument can be summarized as follows. At the beginning of the growth, nucleation centers form [Fig. 3(a)]. Then, each center grows by catching the monomers falling inside its "capture zone", roughly identified with its Voronoï polyhedron. Therefore its size is, at any time, proportional to the surface of its Voronoï polyhedron, which does not change with time (if one neglects nucleation of new islands in the case of homogeneous nucleation). The result is that at any coverage the size distribution of the islands reproduces that of the Voronoï cells, which explains the rescaling for different coverages. We show in Fig. 5 that the scaling of the size distributions also occurs when clusters are allowed to move, but the universal function is different from that found when only monomers move. Three different diffusion hypothesis have been made: only monomers move, monomers and dimers diffuse,



**Fig. 5** Rescaled island size distributions. The island distributions are transformed to  $p(s)$  which represents the probability that a randomly chosen cluster belongs to an island containing  $s$  clusters.<sup>8</sup> The island size  $s$  is scaled by the mean island size  $s_m$ . Sets (1) to (3) correspond to simulations where only monomers are allowed to move ( $\gamma = \infty$ ). For sets (4) to (6),  $\gamma = 1$  but only dimers can move, while for sets (7) and (8) clusters containing up to 100 monomers can move. The detailed parameters used for each set are as follows: (1)  $\phi = 10^{-8}$ , coverage 0.3; (2)  $\phi = 10^{-8}$ , coverage 0.15; (3)  $\phi = 10^{-9}$ , coverage 0.1; (4)  $\phi = 10^{-9}$ , coverage 0.05; (5)  $\phi = 10^{-9}$ , coverage 0.1; (6)  $\phi = 10^{-8}$ , coverage 0.3; (7)  $\phi = 10^{-8}$ , coverage 0.15; (8)  $\phi = 10^{-8}$ , coverage 0.05; (9)  $\phi = 10^{-8}$ , coverage 0.1. The lines represent averages of the distributions for each case.

all clusters up to size 100 do move ( $\gamma = 1$  has been taken in the two last cases). We see that the universal function becomes narrower and has a higher maximum when larger and larger clusters are allowed to diffuse.

## 5. DISCUSSION AND CONCLUSION

In summary, we have proposed a model that describes the diffusion-controlled aggregation exhibited by particles as they are deposited on a surface. The model, which incorporates deposition, particle and cluster diffusion, and aggregation, closely reproduces some experimental images [compare Figs. 1(a), 1(b) and Figs. 3]. We find that the model permits one to distinguish the effects of deposition, diffusion and aggregation, and that tuning the relative strength of, e.g., deposition and diffusion, generates a rich range of morphologies — including diffusion limited aggregation, cluster-cluster aggregation, and percolation. The length and time scales characterizing these morphologies depend on such experimentally-controllable parameters as deposition flux and diffusion constant, raising the possibility that the model may prove useful in future studies seeking the controlled design of nanostructure morphologies. we can argue that the DDA model is suited for

- (1) MBE by taking large  $\gamma$  values.
- (2) Other deposition experiments where edge diffusion is absent, for example, aggregate deposition.<sup>12</sup>
- (3) All the dynamic properties related to *small* cluster diffusion on surfaces such as those presented in Sec. VI.

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