Abstract

In an attempt to find generic features on the fractal growth of Au films deposited on Ru(001), a simple simulation model based on irreversible diffusion-limited aggregation (DLA) is discussed. Highly irregular two-dimensional dendritic islands of Au particles that gradually grow on a larger host lattice of Ru particles and have fractal dimension $d_f \approx 1.70$ each, are generated via a multiple ad-hoc version of the DLA algorithm for single aggregates. Annealing effects on the islands morphology are reproduced assuming different sticking probabilities at nearest-neighbour lattice sites of Au films on Ru(001). Using simulation data, islands growth are described in analogy to diffusion-limited, precipitate growth with soft impingement of precipities. This leads to analyse thin film island growth kinetics in such fractal systems and to predict a main peak in scattering intensity patterns due to interisland interference.
Growth model of Au films on Ru(001)

E. Canessa and A. Calmetta

ICTP-International Centre for Theoretical Physics
Condensed Matter Group
P.O. Box 586, 34100 Trieste
ITALY
The two-dimensional (2D) thin film growth on single-crystal surfaces is being a subject of considerable interest \[1, 2\]. Particularly so are the recent experimental investigations on Au thin-films deposited on Ru(001) which have revealed novel and intriguing phenomena \[2\]. Upon deposition at room temperature, it has been found that highly dendritic Au islands (one layer thickness and width of approximately 100 Å) nucleate on several larger Ru terraces to form fractal aggregates with an average fractal dimension \(d_f \approx 1.72 \pm 0.07\) each. Hence, such dendritic island shapes are believed to be due to diffusion-limited aggregation (DLA) mechanism \[3\]. Upon annealing to 650 \(K\), the islands are seen to collapse into compact forms.

Despite theoretical efforts over the last decade in the area of single fractal structures (see \(e.g.\) \[4, 5, 6\]), the natural extension of phenomena to the ‘simultaneous’ growth of 2D dendritic islands diffusing on multiple terraces is hampered by the complexity of this problem. The presence of several moving interfaces, whose local velocities may be in turn determined by the normal gradient of the Laplace field on each island \[7\], is not readily amenable to modern theories \[6, 8\] especially so because of the complex boundary conditions. An alternative to understand these aggregation phenomena consists of applying the DLA simulation approach of Witten and Sander \[3\] to model the gradual grow of aggregates by the successive addition of random walkers to the perimeter sites of (many) forming islands. This is the aim of this letter.

In an attempt to find generic features on the fractal growth of Au films deposited on Ru(001), we shall report the results of a simple simulation model based on irreversible DLA. Via a multiple \textit{ad-hoc} version of the DLA algorithm, we generate (13) highly irregular two-dimensional dendritic islands of (Au) particles that gradually grow on a larger host lattice of (Ru) particles and, even more important, present fractal dimension \(d_f \approx 1.70\) each. We mimic the annealing effects on the (several) clusters morphology by assuming different sticking probabilities at nearest-neighbour lattice sites of Au films on Ru(001) \[3\]. From the results of simulations, which are shown to display relevant
experimental features, we predict a main peak in scattering intensity patterns due to the fact that the average edge-to-edge island spacings are less than or equal the average island diameters.

The multiple DLA simulation model we use starts by locating 13 seed particles at the corners, edges and (sheared) centers of two concentric squares which in turn are contained on a third, larger 2D square lattice. The chosen sites of the larger host lattice shall represent the positions of the Ru particles.

Following previous simulations [5, 9], we then add spherical Au particles one at the time undergoing a random walk starting from a point on a variable circle centered on the intersection of both squares (containing the central seed particles). As a difference, however, in our case the radii of such circles change according to the distance from the squares’ center to the most distant particle in the (outer) growing islands in which several (Ru) seed particles are also contained. If in this process the Au particles, that are being deposited adjacent to (occupied Au or Ru) lattice sites, reach a point that is larger than a few times the diagonal of the smaller square, then these are not longer included. We started of again the random walk at a nearest randomly chosen position remembering that the variable circles enclose the growing clusters untill eventually they cover all thirteen. This means that islands are only allowed to growth gradually starting from the centre of the square lattice for simulations towards the corners of the square containing the outer four (Ru) seed particles.

Although this stochastic model we are proposing for modelling the present phenomena may be seen as heuristic, we shall show next that, in fact, by using this algorithm the fractal growth of all inner islands contained around the central one becomes essentially ‘simultaneous’. In our new application of the DLA model to the fractal growth of Au on Ru(001), we shall also see below that sticking probabilities less than unity (corresponding to DLA) on island formation will allows to reproduce nicely the annealing effects as seen experimentally. The radius of gyration for each island will be here related to the number
of particles contained in such single clusters by

\[ R_{g}^{(n)} \sim N^{1/d_f} \quad n = 1, 2, 3, \ldots , \] (1)

where \( d_f \) is the Hausdorff (fractal) dimension of the \( n \)-island having a size which is large enough.

We now focus on the results of our stochastic ad-hoc DLA version. An example of the structures generated by computer is shown in Fig.1. This figure shows 13 irregular 2D dentritic islands of (Au) particles that gradually grow on a larger host lattice of (Ru) particles. The total number of deposited (Au) particles is 2200 in a 260 \( \times \) 260 square lattice. The islands contain more than 100 particles each. The (different) arrival times for the first 1100 added particles are represented in Fig.1 using open dots. This distinction also enables to show that the fractal growth of all inner islands contained around the central one becomes almost ‘simultaneous’.

Model particles are added one at the time to a particular DLA island, that are contained well inside the edges of the simulation box, via random walk trajectories that have originated from the fluctuating inner region compressed between the central growing cluster and the corresponding square edges (also shown in Fig.1). Let us see below how these irregular island shapes may be removed from their thermal stability.

In order to reproduce annealing effects on the clusters morphology, Fig.2 shows the results of our DLA-based model simulation of the 13 irregular dentritic islands as in Fig.1 but assuming a sticking probability of \( s \approx 0.17 \) at nearest-neighbour positions only. These new islands contain more than 400 particles each and in total sum up 8600 particles. The arrival times in this case for the first half of added particles is also represented in Fig.2 by full dots.

It is evident from Fig.2 that different sticking probabilities on island formation lead to reproduce smoother structures as seen experimentally [2]. Since we have assumed for simplicity that there is no mass transfer between Au islands more extended and connected structures can not be formed. This suggest that these dendritic forms growing
with a sticking probability different from 1 \(i.e.\) DLA are related to the diffusion of Au particles not being stick on each contact. As in the case of single clusters reported in the literature \[9\], in our study a small sticking probability also leads to generate denser islands.

We examine next the fractal properties of the simulated fractal islands displayed in Figs. 1 and 2. We count the number of particles \(N(r)\), c.f. Eq.\((1)\), inside a circle of increasing radius \(r\) (in lattice units) around each (Ru) seed particle and plot it as a function of \(r\) in a log-log plot as depicted in Fig. 3(a), (b) and (c). These curves corresponds to Au particles inside the circles centered at (a) the four corners of the outer squares in Figs. 1 and 2 (drawn with solid lines), (b) the center of the four edges of the outer squares in Figs. 1 and 2 (drawn with solid lines), (c) the four corners of the inner squares in Figs. 1 and 2 (drawn with dashed lines).

For comparison, in Fig. 3 the functions \(N(r)\) for the central islands along the intersection of the diagonals of both squares in Figs. 1 and 2 are also plotted (using connected dots) throughout 3(a), 3(b) and 3(c). These results have been obtained by adding up to about 1500 particles to the single central clusters in the absence of any other seed (Ru) particle. It can be immediately concluded that, to a good approximation, the simulated 2D dentritic islands reveal DLA fractal dimension \(d_f \approx 1.70\) \[3, 10, 11\] for almost one decade in Fig. 3. The central DLA cluster of Fig. 1 leads to lower values of \(\ln N(r)\) than the central DLA cluster of Fig. 2 for a fix value of \(\ln r\) but both slopes are found to be parallel. These interesting findings encourages us to give a further justification to our simulation model which allows the fractal islands to growth gradually from the centre of the simulation box towards the four corners of the square containing the outer (Ru) seed particles.

Using the present algorithm for the stochastic simulation, it becomes thus possible to generate highly irregular 2D dentritic islands in reasonable accord with observations of Ref.\[2\]. Fractal dimensionality in such set of complex patterns all present DLA-\(d_f\).
This is important considering that 13 irregular islands grow almost ‘simultaneously’. These results seem to reflect the essential physics behind these complex phenomena, namely, the growth being dominated by Au particles migrating via random walks over the Ru surface. Since contributions to the random growth process from the spherical (Au) particles in the central region become extremely small on successive increasing of the amount of fractal islands, this may -to some extent- be a way of taking into account the presence of kinetic limitations existing at room temperature in thin-film growth. In fact, further insight on changes of the average island radius with ‘time’ can be obtained as discussed next.

For 2D random walks, the mean squared distance made by particles during a given time interval \( t \) satisfies \( < r^2(t) > \sim t \). Therefore, when measuring the extend of Brownian trajectory by the total number of places visited by a particle making \( t \) steps, the above is equivalent to

\[
N(r) \sim < r^2(t) > \sim t .
\]

(2)

This relationship between \( t \) and the number of particles covering a circle of radius \( r \), enables us to analyse the islands growth in analogy to diffusion-limited, precipitate growth with soft impingement of precipities \[12\]. In drawing this analogy, we follow Ref.\[12\] and consider immobile Au-islands growing on Ru(001) as the precipitates. As a difference, in this work we concern ourselves with experiments on fractal growth of 2D Au islands on Ru(001) \[2\], whereas in Ref.\[12\] Au-atoms were deposited on glass substrates forming (rather circular) island films. In both measurements, however, evidence of island immigration processes (or mobility) has been found upon annealing.

Assuming the area in the island migration process to be conserved, then thin film island growth kinetics can -to a crude approximation- be described in terms of post-deposition island growth. Thus, the growth of nucleated precipitates can be described
by the stretched exponential response: \[ 12 \]

\[
\left( \frac{r(t)}{r_o} \right)^3 = 1 + R[1 - e^{(-t/T_0)^m}] ,
\]  

(3)

where \( r(t) \) is an average island radius at time \( t \) and \( r_o \) is the initial radius, \( T_o \propto e^{Q/k_BT_o/D_o} \) is a time constant proportional to the island diffusion coefficient \( D_o \) and migration activation energy \( Q \), and \( R \) is the fractional island size increase at \( t \to \infty \).

In the above the dimensionless exponent \( m \) equals 1 because the random walk diffusion of single particles (until they reach the growing fractal clusters) is confined to 2D. So, in the present case, the stretched exponential relaxation of Eq.(3) does not differ from a simple exponential law. For post-deposition island growth, surface diffusion is confined to 2D and island growth occurs in 3D \[ 12 \].

In order to give a simple estimate of the ‘time’ variations of the average island radius we use next the results of our multiple DLA growth model, (c.f. Eq.(1)), in conjuction with relations (2) and (3). In doing this, we have that islands execute Brownian motion at a given temperature and time. Figure 4 shows results obtained using our simulation data for the central irregular 2D-DLA island of Fig.1. Similar results are found when considering the 12 nearest islands or, alternatively, those of Fig.2. This is because, as we have shown in Fig.3, the slopes are to a good approximation all parallel.

As a result of island mobility due to atomic motions in the islands it can be shown that the relation \( r(t)/r_o = h_{pl}/h_p(t) \) holds, where \( h_{pl} \) is the initial peak position of scattering patterns and \( h_p(t) \) is the position at a given succesive time \[ 12 \]. Then, we are able to predict that in the fractal growth of Au films deposited on Ru(001), there should be a main peak in (small angle) scattering intensity data due to the fact that the average center-to-center island spacings are of the order of average island sizes. This phenomenon being also observed in the circular islands growth of Au-atoms deposited on glass substrates. From the curves in Fig.4, that characterize the growth and post-deposition ‘kinetics’ of our simulated Au-thin film islands on Ru, we also argue that there should be a rapid increase in island sizes followed by a plateau region. As a first order
approximation, this plateau should decrease when increasing the migration activation energy assuming the single atom diffusion coefficient $D_o$ to be constant in 2D.

In this way we have taken the first steps towards understanding multiple fractal growth of 2D islands. A simple model based on irreversible DLA has been introduced inspired by the properties of fractal growth of Au films deposited on Ru(001). Discrete 2D dendritic islands of Au atoms that grow on a larger host lattice of Ru atoms, having DLA fractal dimension each, were generated via an extended version of the DLA algorithm for single aggregates. Annealing effects on the islands morphology were reproduced assuming different sticking probabilities at nearest-neighbour lattice sites. From these simulations, the islands growth were described in analogy to diffusion-limited, precipitate growth with soft impingement of precipitates. This allowed us to analyse thin island growth ‘kinetics’ of Au films on Ru(001) and predict a main peak in (small angle) scattering intensity pattern. As a main difference with respect to gold islands on glass substrates [12], fractal growth of Au films on Ru(001) is dominated by particles migrating (only) via random walks over a surface of several seed obstacles. In addition, we may also make variations of the model, e.g., to include random (Ru) defects or generate a larger amount of islands, but to achieve this larger scale simulations are needed.

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Figure captions

- **Figure 1**: DLA-based model simulation of 13 irregular 2D dendritic islands of (Au) particles that gradually grow on a larger host lattice of (Ru) particles.

- **Figure 2**: DLA-based model simulation of 13 irregular dendritic islands as in Fig.1 but assuming a sticking probability of $s \approx 0.17$ at nearest-neighbour positions only.

- **Figure 3**: Number of spherical particles $N(r)$ inside a circle of radius $r$ centered at (a) the corners of the squares in Figs.1 and 2 (full lines), (b) the edges of the squares in Figs.1 and 2 (full lines), (c) the corners of the squares in Figs.1 and 2 (dotted lines). The $N(r)$ values for the central islands, lying on the intersection of the square diagonals of Figs.1 and 2, are plotted by (connected) black dots throughout (a), (b) and (c).

- **Figure 4**: Exponential response of the reduced average island radius $[(r(t) / r_o)^3 - 1] / R$ at ‘time’ $t$ and different time constant $T_o$ proportional to the island diffusion coefficient and migration activation energy.