JOŽEF STEFAN INSTITUTE
JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL
PROGRAM NANOSCIENCE AND NANOTECHNOLOGIES
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Barbara Horvat

Diffusion Limited Aggregation and Thin Films

Seminar at Prof. Dr. Barbara Malič

Mentor:
Asst. Prof. Dr. Goran Dražić

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1 Introduction

I was introduced with aggregation when I started dealing with nanomaterials especially nanotubes. Aggregation represents a major problem because single tube is needed when testing its properties, when observing it under transmission electron microscope (TEM)... The best theory to described observed phenomena is diffusion limited aggregation (DLA), introduced in 1981 by T. A. Witten and L. M. Sander, which is used to describe growth of fractals (see Chapter 1.1). But not just fractals from a single point and not just in two dimensions i.e. this phenomena was also observed in growth of thin films.

1.1 Fractals

Fractals are irregular shapes that can not be represented by classical geometry. Its pattern is repeated at ever smaller scales i.e. fractals are self-similar. In contrast to regular shapes (triangles, squares...) fractals have non-integer dimension D. There are several examples of fractal-like structures in living as well in nonliving nature: mineral deposition, snowflake growth, fjords made by glaciers, corals, lichen etc. (see Figures 1 and 2).

Figure 1: There are numerous examples of fractal-like structures from nature: tree's crown and roots, branches...

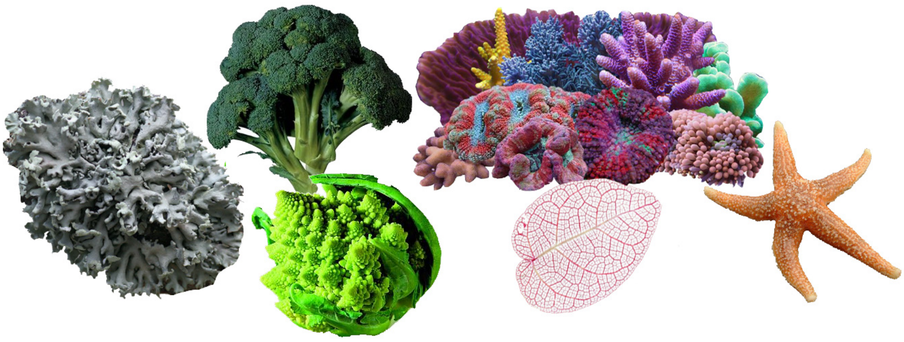

Figure 2: Not just plants have the possibility to grow fractal-like (lichen, broccoli, leaf's venation), there are also some interesting examples of fractal-like animals (corals, starfish).

Fractional dimension D is a statistical quantity that gives an indication of how completely fractal fills space

$$D = -\frac{\ln N}{\ln r}, \tag{1}$$

where N is number of objects, which build the fractal, with a characteristic linear dimension r [1].

1.2 Thin films

Thin film is thin material layer deposited onto a metal, ceramic, semiconductor or plastic substrate. Its thickness varies from fractions of a nanometre to several micrometers.

Newer thin-film deposition technique is hydrothermal synthesis. With high pressure and temperature in autoclave particles from suspension are deposited onto the substrate. In experiments done in our laboratory, thin layer was so attached to the surface that it is believed that thin layer starts to grow from the substrate out i.e. Ti in the substrate represents the nuclei for growing/depositing structure (See Figure 3).

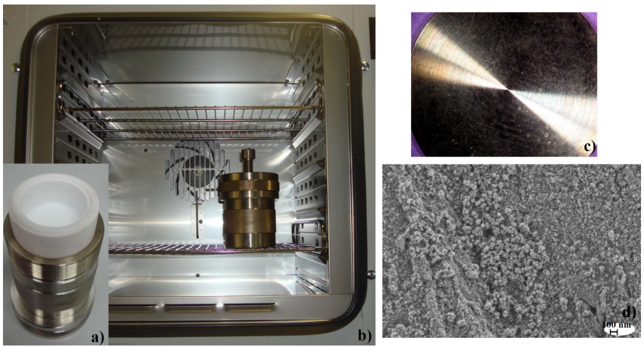

Figure 3: a) Autoclave with the initial suspension. b) Autoclave in furnace. c) Thin film of anatase TiO_2 grown on a substrate Ti6Al4V. d) Thin film observed under field emission gun scanning electron microscop (FEG-SEM).

2 Diffusion Limited Aggregation

If particles have the possibility to attract each other and stick together, they form aggregates ("Aggregation" in DLA). Driving force of non-charged particles before sticking to the aggregate is diffusion i.e. Brownian motion ("Diffusion" in DLA). Diffusion is the macroscopic result of random thermal motion on a microscopic scale. If the distribution of all types of particles in the solution is not uniform, there will be a net flux $\vec{j}$

$$\vec{j} = -D\vec{\nabla} n, \tag{2}$$

where D is diffusion constant and n concentration (molar or molecular). Equation 2 is called Fick's law. Diffusion equation which includes sources q and has a constant D yields

$$\frac{\partial n}{\partial t} = D\nabla^2 n - q. \tag{3}$$

DLA is "Diffusion-limited" because the particles are considered to be in low concentrations so they don't come in contact with each other and the structure grows one particle at a time rather then by chunks of particles.

DLA-structures (see Figure 4), Brownian trees, are fractal aggregates made by DLA, where the shape of the cluster is controlled by the possibility of particles to reach the cluster via Brownian motion. The aggregates grow as long there are particles moving around. “Arms” of the cluster “catch” particles so that they can’t reach inner parts of the cluster. During the diffusion of a particle through the solution it is more likely, that the particle attaches to the outer regions than to the inner ones of the cluster.

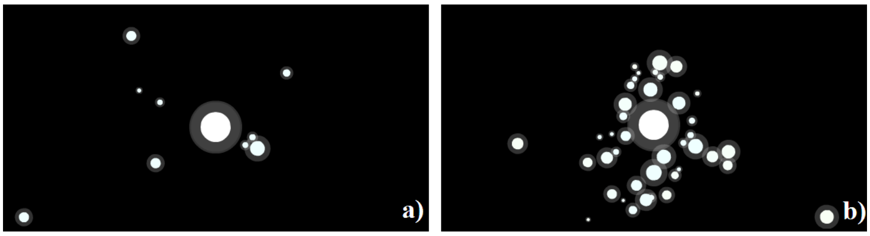

Figure 4: Growing DLA-cluster. a) There are just few particles moving around initial particle located in the centre. b) After some time fractal-structure starts to appear [2].

A single-particle bump on a straight edge of the cluster is more likely to catch a wandering particle also due to the fact that it has three unoccupied neighbours while each particle along the edge has only one unoccupied neighbour (see Figure 5).

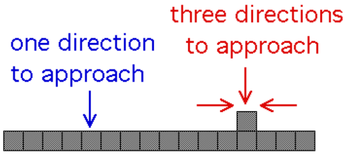

Figure 5: Higher probability to glue to the cluster onto the bulk goes to more unoccupied [3].

Existence of the linksticking coefficient can’t be avoid i.e. when a particle reaches the cluster it will not always stick. Thus, when it doesn’t stick immediately, it moves along in the vicinity of the cluster’s arms, until it either finally sticks somewhere or gets lost. If the wandering particle strikes part of the existing structure and always sticks, then stickiness is 1. Otherwise is less then 1. Low stickiness probability gives rise to denser clusters.

There are also different attaching probabilities depending on the current geometrical environment i.e. the more neighbours are already present, the more likely it is for a particle to attach.

Number of main branches depends on a lattice: square lattice has four closest neighbours i.e. it has four main branches, triangular lattice has six closest neighbours i.e. it has six main branches (observed in snowflakes). Final structure depends also on the initial conditions (see Figure 6) i.e. whether fractal growth starts from a point, a line. . . DLA becomes diffusion-limited deposition (DLD).

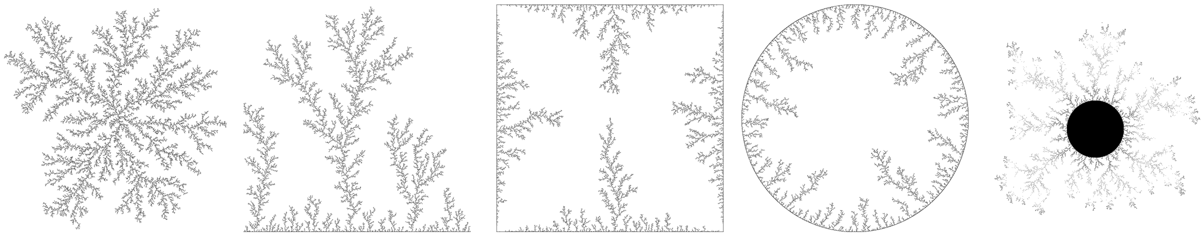

Figure 6: Initial seed is point, line, inner part of a square, inner/outer part of a circle [4].

Fractal growth has been observed after certain growth time under field emission scanning electron microscope (SEM) which gave direct proof of the DLA process (see Figure 7).

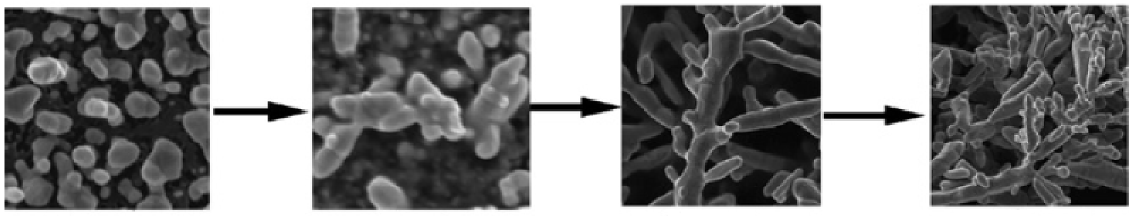

Figure 7: The growth-time dependent morphology of the silver structures, demonstrating DLA process. The growth time is 1, 5, 10 and 60 min from left to right [5].

The dynamics of deformable bodies with a well defined surface can be represented by a gauge field Ψ [6]: inside the body is $\Psi \leq 0$, outside $\Psi > 0$, on the surface, which grows by deposition of diffusing particles, is

$$\Psi(x, y, z; t) = 0. \tag{4}$$

Taking into account diffusion equation 3, a certain rate of absorption per unit time at a given boundary point i.e. velocity field of growth of the structure, it is possible to write equation of motion of Ψ (changing of surfaces topology)

$$\frac{\partial \Psi}{\partial t} - \lim_{\epsilon \to 0^+} D \int dt' d\vec{r}' \vec{\nabla} G(\vec{r} - \vec{r}', t - t') \cdot \vec{\nabla}\Psi(\vec{r}, t) \frac{\partial \Psi}{\partial t'}(\vec{r}', t') \delta[\Psi(\vec{r}', t') - \epsilon] = -\frac{1}{n_0} D \vec{\nabla} n^s \cdot \vec{\nabla}\Psi. \tag{5}$$

where n^s is the concentration that would have existed just in the presence of the sources, n_0 is the concentration of the growing structure, G is the Green function. Solution of the equation 5 gives the description of the surface growth.

2.1 DLA and thin films

There were several reports on DLA growth of thin films [7, 8, 9]. One of the methods where fractals successfully grew on the substrate is using bulk selenium (Se) powder and silver (Ag) foil in a solvothermal process in autoclave at 160 $^\circ C$ for 10 h with alcohol as a solvent [7]. Dendrites of Ag_2Se nanocrystals were formed, with each dendritic branch often in single-crystal form and nearly all branches having their (001) crystal direction pointing along the surface normal of the Ag foil substrate. The Ag_2Se reaction product aggregated first into nanoparticles that were solvated.

The diffusion and DLA of these nanoparticles gave rise to the formation of dendrites from an Ag nanowire (see Figure 8). Similar to this case is when replacing Ag nanowire with Ag foil (see Figure 9): arrival of Se to the silver surface, the formation of Ag_2Se and the nucleation of Ag_2Se nanocrystals. Different from the formation of Ag_2Se nanocrystals on a Ag nanowire, the formation of Ag_2Se nanocrystals on a Ag foil is supported by surface energy minimization toward the formation of Ag_2Se nanocrystals with their (001) crystal orientation preferentially aligned with the normal direction of the flat surface. Even more, the diffusion of the Ag_2Se nanocrystals is also mediated by the flat surface, which leads to the tendency of forming 2D dendrites parallel to the flat surface. The diffusion of Ag_2Se nanocrystals on top of first layer of 2D dendrites leads to the growth of the dendritic film in a 3D island growth mode (see Figure 10).

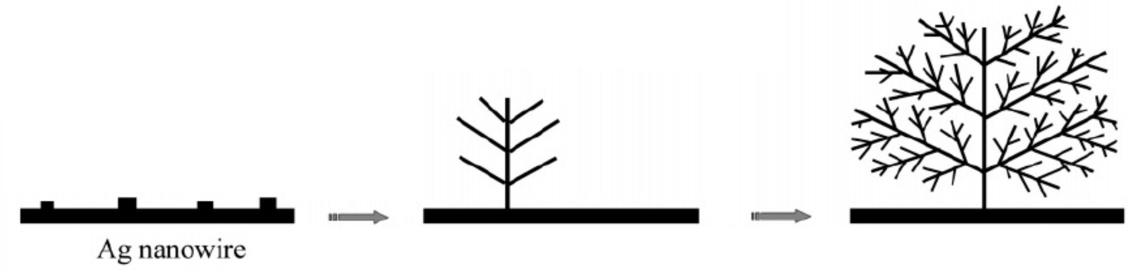

Figure 8: Schematic diagram of the Ag_2Se dendrite growth mechanism from an Ag nanowire with no surface-mediated support [7].

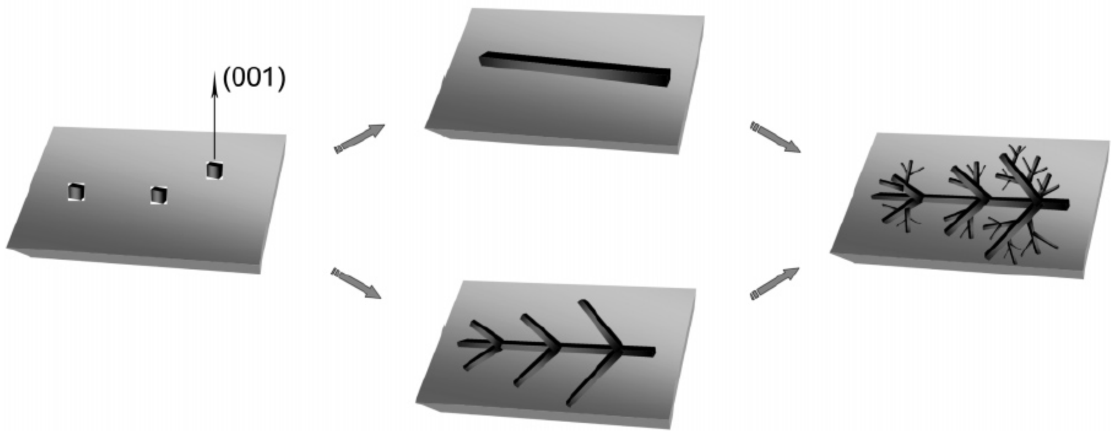

Figure 9: Schematic diagram of the Ag_2Se dendrite growth mechanism from an Ag foil with surface-mediated nucleation to enable (001)-oriented dendrite growth [7].

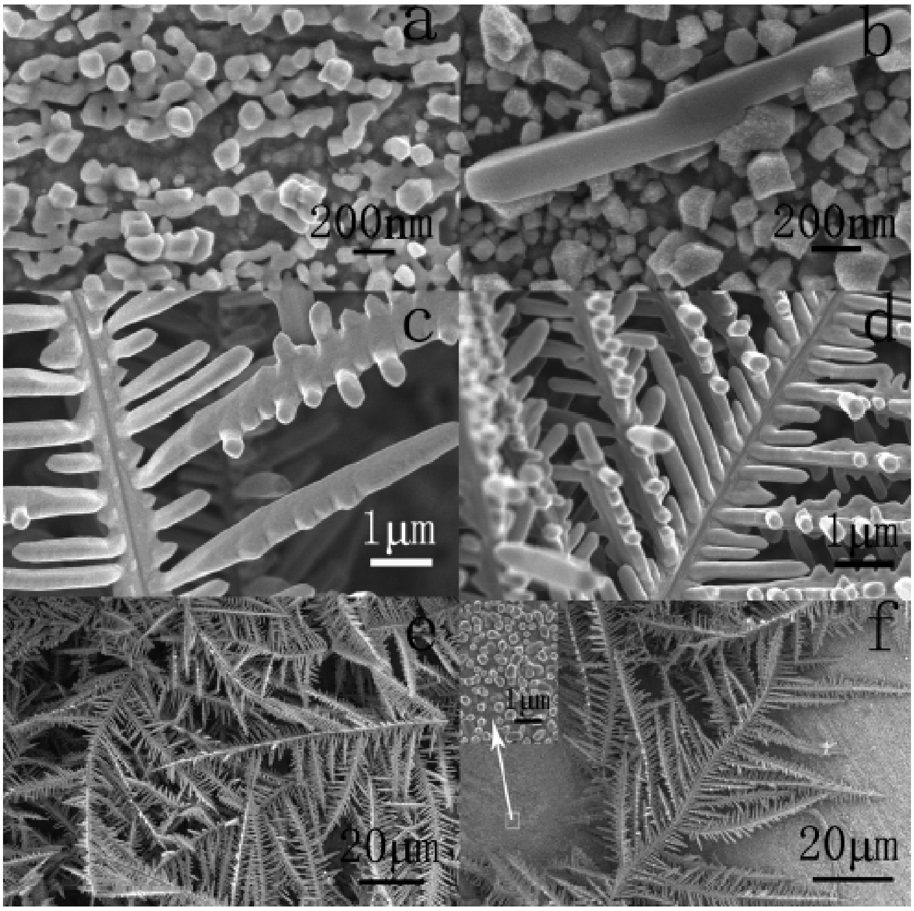

Figure 10: SEM morphologies: a) nanocrystals of (001)-oriented Ag_2Se after 1 h of solvothermal growth with methanol as the solvent; b) oriented attachment toward the formation of the trunk of a dendrite after 3 h of solvothermal growth with methanol as the solvent; c) close-up of a full dendrite formed after 12 h of solvothermal growth with methanol as the solvent; d) close-up of a full dendrite formed after 12 h of solvothermal growth with dodecanol as the solvent; e) large-field view of dendrites formed under the conditions of part -c- for the case of a relatively high nucleation density; f) large-field view of dendrites formed under the condition of part -d- for the case of a relatively low nucleation density [7].

Another method for growing fractals on film from literature is on a thin porous silicon layer which was immersed in a 2.5 M NH_4F solution containing 0.01 M silver nitrate ($AgNO_3$) at 50 $°C$ (see Figure 11) [8]. After the etching process, the silicon wafers were cleaned. In NH_4F solution, the etched silicon substrates were always wrapped with a layer of thick silver film, which was rather loose and could be easily detached from the surface of silicon substrates. A morphological evolution of silver dendrites was followed by a time-dependent process (see Figure 12).

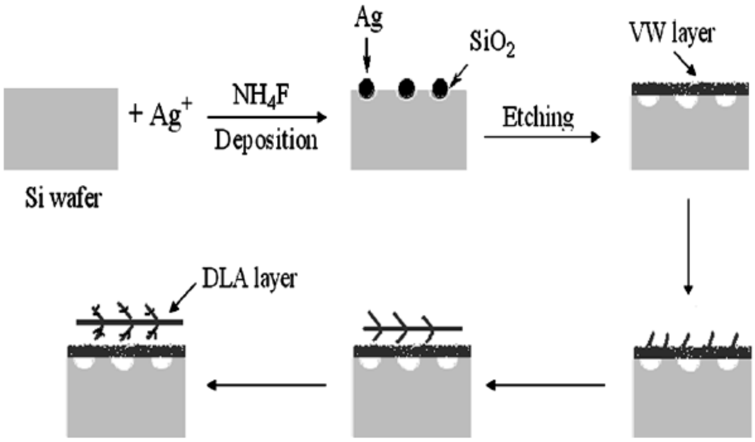

Figure 11: Schematic illustration of the growth process of silver dendrites [8]. The layer of a silver nanoparticles/nanoclusters and the layer of synchronized silver dendrites were named as the Volmer-Weber (VW) layer and the DLA layer respectively. DLA layer derived from the continuous aggregation growth of small particles on the VW layer.

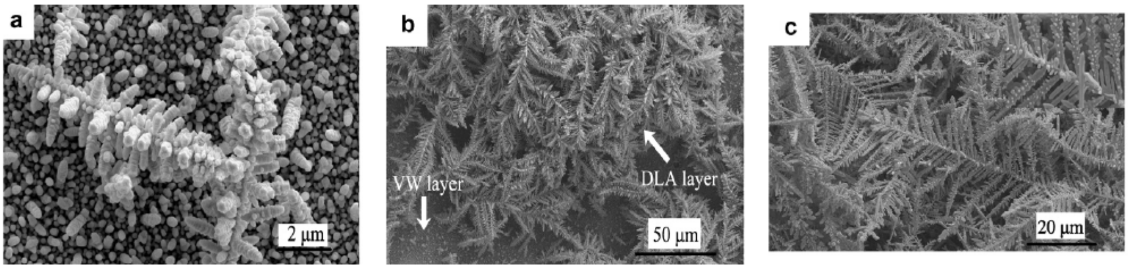

Figure 12: SEM images of the silver films prepared in a 2.5 M NH_4F solution containing 0.01 M silver nitrate at 50 $°C$ for a) 5 min B9 15 min and c) 60 min [8].

3 Conclusion

On the web there are numerous programs and interesting simulations of DLA growth of fractals. There are even some lectures about mathematical fractals. However, non-mathematical/experimental growth of fractals i.e. DLA was proven with observing growth of the silver structures under SEM. It has to be memorized that density of particles should be low enough because diffusion in fractal growth should represent the main transport. Sometimes we want to avoid aggregation, especially cluster-cluster aggregation. To avoid this phenomena the density of particles should be so low, that only few clusters can form.

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