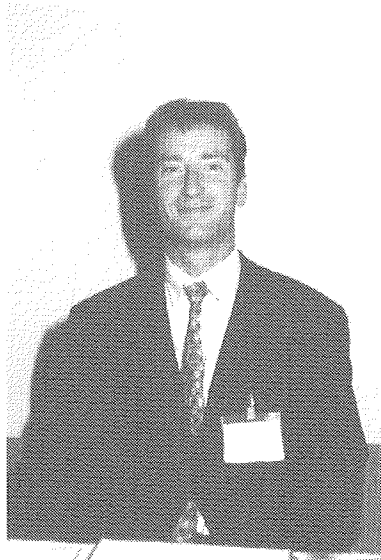


**MICROSCOPIC VIEW  
OF NUCLEATION  
AND AGGREGATION  
ON METAL SURFACES**



**DR HARALD PETER BRUNE**

*Dear Dr Latsis,  
Prof. Thorens,  
Ladies and Gentlemen,*

It is a great honor for me to be awarded the Latsis Prize 1996 and I would like to express my deepest gratitude to the Latsis family and their foundation. It is a great pleasure for me to have the opportunity to give insight into the key issues of my research activities performed at the Ecole Polytechnique Fédérale de Lausanne in the following presentation under the title:

## **MICROSCOPIC VIEW OF NUCLEATION AND AGGREGATION ON METAL SURFACES**

### **Introduction**

There has always been a great interest in a detailed understanding of thin film growth. Partly this interest is due to manifold technological applications like, e.g., magnetic/nonmagnetic sandwich structures for magnetic data storage, metal coatings and contacts in semiconductor devices, or, for instance, thin films of a magnetic metal that may be used as a spin filter for electrons in order to produce polarized electron beams. These applications commonly rely upon the capability to grow thin metal films of the desired morphology and abrupt interfaces in a controlled way. In the thermodynamic limit, the growth morphology of a metallic film is determined by the balance of the surface and interfacial free energies involved. In most cases, however, thin films are grown under conditions far from equilibrium. Their morphology is then determined by the kinetics of epitaxy. A full understanding of film growth therefore requires the study of the atomic processes involved in metal epitaxy. For the submonolayer regime these include the adsorption of atoms from the vapor phase and their subsequent

diffusion on the substrate surface. This is followed by nucleation, which occurs when diffusing adatoms meet each other, and further by island growth until finally their coalescence sets in. For multi-layer growth it is decisive whether adatoms that impinge on-top of islands are able to descend at steps. The potential they feel at steps can reveal an additional barrier which may hamper their descend and provoke three-dimensional growth. On the other hand, perfect completion of successive layers, i.e., layer-by-layer growth, takes place if they descend at least as fast as they arrive.

The study of the microscopic diffusion processes has been one of the central issues of my recent research. In order to have access to the kinetics of the relevant atomic processes, scanning tunneling microscopy (STM) has been developed for variable sample temperatures (25K - 800K) in ultra high vacuum. In fact, the kinetics of any physical process or chemical reaction taking place on a surface can be studied in real space and on an atomic level by extending STM to variable temperatures. Application to metal epitaxy opened up an unprecedented microscopic view of nucleation and aggregation on single crystalline surfaces. Several methods to extract the parameters governing kinetic film growth from variable temperature STM data have been developed. The most important results are summarized below.

Apart from a basic understanding of film growth there is a second, more fundamental interest in the kinetics of metal epitaxy motivated by the recent discovery of various patterns that form during two-dimensional metal aggregation at low temperature. The shape of these aggregates is determined by the mobility of the aggregating particles after their first impact to the growing cluster. Interestingly pattern formation on crystalline surfaces revealed a quite similar behavior as observed for other non-equilibrium growth processes in nature. For example, a transition from randomly ramified fractal aggregates

to dendritic, snowflake like, symmetric islands was observed. In complete analogy to electrochemical deposition experiments the transition in shape could be induced by a variation of the growth speed. The central question, what causes some patterns to be dendritic and others to be solely dominated by random, could be addressed for the present system of two-dimensional metal aggregation. The mechanism responsible for dendritic growth on hexagonal metal surfaces has been identified. Results obtained on diffusion limited metal aggregation will be discussed in more detail below.

Since nucleation and aggregation have been studied in great detail, and, in course of these studies, several patterns with intriguing properties have been observed to form, it was tempting to create metallic structures with well defined shape, dimension and nanometer size by means of self organized epitaxial growth. This led to the development of a new technique of kinetically controlled growth which exploits the energetic hierarchy of the different diffusion and dissociation processes, their dependence on substrate symmetry and on the lattice strain inherent in heteroepitaxial systems. In contrast to methods relying on atom manipulation, where only one structure can be built at a time, the self organized growth of nanostructures exploits the laws of nature to create the desired structures in great abundance at once. Even though, their morphology cannot be chosen arbitrarily, they offer the great advantage that, due to their density, their electronic, magnetic and chemical properties can conveniently be studied by means of conventional integrating techniques. First examples of structures assembled that way are Ag islands with fractal and integer dimension on Pt(111) with desired density and average size and monoatomic Cu wires on Pd(110).

## Nucleation

Nucleation refers to the process that atoms which have been evaporated from the vapor phase onto the substrate diffuse around and meet each other and form a nucleus. This nucleus then either dissociates or may rest stable upon reaching a certain size (one atom below this size is called the *critical size*). In course of deposition the number density of nuclei steadily increases until they reach a density where arriving atoms rather diffuse towards an existing nucleus than create a new one on the area of free substrate in between. At this state the density of nuclei saturates (*saturation island density*) until it finally decreases due to coalescence. The saturation island density is hence a measure for the mean free path of adatoms at a certain deposition flux and should obey an Arrhenius behavior, since diffusion does. This is indeed the central prediction of classical mean-field nucleation theory [1].

Our variable temperature STM studies allowed for the first time to directly verify the scenario described above from the very initial stages of nucleation up to the coverage regime of coalescence [2]. The experiments were carried out for Ag/Pt(111) at temperatures where Ag dimers are stable, i.e., the critical nucleus is a single atom. The stability and immobility of dimers could be tested in independent experiments, either upon annealing [3] or by looking at the size of the first stable nuclei that form. That dimers are stable largely simplifies nucleation theory and therefore enables its quantitative test. The experiments confirmed exactly the predicted Arrhenius behavior and rate dependency of the saturation island density and are thus a proof of nucleation theory. Its application to island densities obtained from STM measurements, in turn, enables to measure the activation energy and attempt frequency for surface diffusion.

The method developed for measuring migration activation barriers for surface diffusion from studying nucleation densities as a function of temperature, meanwhile became an established technique. It was successfully applied to various systems within our group (Ag/Pt(111) [2], Ag/Ag(111) [4], Cu/Pd(110) [5], Cu/Ni(001) [6], Al/Au(111) [7]) as well as recently in other research laboratories for Fe(001) [8] and Pt(111) [9] homoepitaxy.

In contrast to field ion microscopy (FIM) experiments the method of using STM to study nucleation as a function of temperature can be applied to real epitaxial layers, in particular to heteroepitaxial systems where strain is involved. It has been argued in theoretical studies that isotropic strain is expected to strongly alter diffusion barriers (see, e.g., [10]). For the system Ag/Pt(111) this question could be addressed experimentally. The first Ag layer, if completed, forms a pseudomorphic (1x1) layer which is under 4.2% isotropic compressive strain due to the lattice mismatch between Ag and Pt. Nucleation on this layer indeed shows drastic deviations from that on Pt(111) and on the unstrained Ag(111) surface [4]. That this effect is due to strain rather than to electronic adlayer-substrate coupling was inferred from calculations with effective medium theory (EMT) in collaboration with the group of Prof. J. Nørskov in Denmark. If strain is accumulated in successive layers it becomes energetically more favorable to relieve part of it in forming partial dislocations [11]. Also in this anisotropic form, strain can strongly alter nucleation densities since dislocations can act as rather effective barriers for diffusing adatoms.

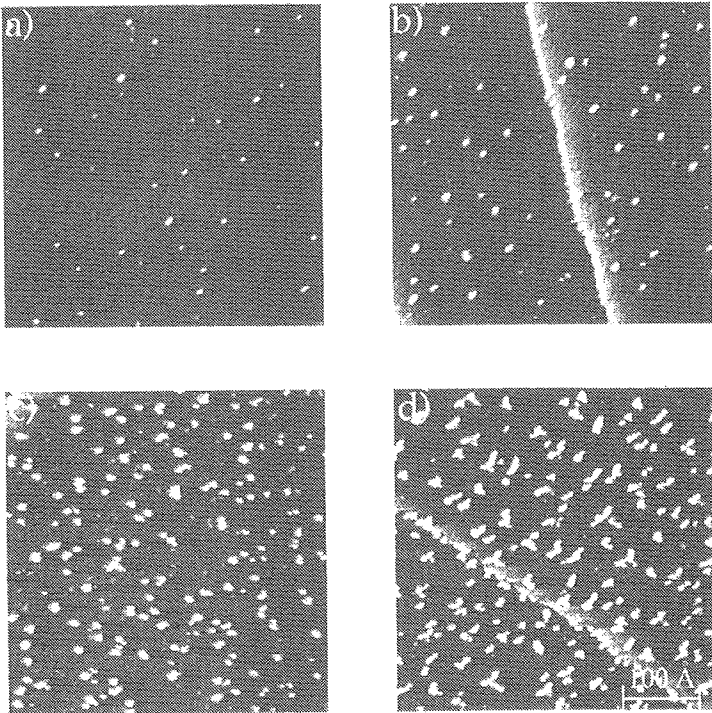


Figure 1. STM images showing the evolution of island size and density in course of Ag deposition onto a Pt(111) substrate held at 75 K. Figs. a) and b): initial stages of nucleation – the density of nuclei (their mean size is only 2.4 atoms) increases proportional to coverage; figs. b) to c): transition from nucleation to growth (mean island size in c) 6.5 atoms). Fig. d): pure growth regime – increasing the coverage solely increases the island size, the island density has saturated.

Recently, there has been a great theoretical interest in noting that island size and distance distributions should satisfy simple scaling laws. These have been verified experimentally for Ag/Pt(111) [12] and Cu/Ni(001) [6]. In the latter case, the transition from post-nucleation, where diffusion is too slow and nucleation occurs after deposition, to the regime where dimers are stable, and finally to that of stable tetramers could be illustrated. The square substrate symmetry causes trimers to have the same stability as dimers, therefore they do not show up in the stability regimes.

Besides the intralayer diffusion and nucleation, a very important kinetic parameter in film growth is the interlayer diffusion, i.e., the activated jump down of an atom from a descending step. That an adatom can encounter an additional barrier when diffusing over a step has early been realized [13]. Again application of mean-field nucleation theory to variable temperature STM data allowed us to measure this barrier. If one deposits atoms on top of islands, there is a rather abrupt transition in island size from where all material deposited on top is able to descend, to the point where nucleation of new islands on-top sets in [14]. We have used this approach to accurately measure the barrier and attempt frequency for jump down [15]. Also in the case of interlayer diffusion strain turned out to strongly influence the barriers. It was seen that compressive strain considerably facilitates interlayer diffusion which can be rationalized since strain can make exchange processes at the island edge more favorable.

These examples illustrate how variable temperature STM can be applied to measure the kinetic parameters that determine the film morphologies with a precision that has so far been obtained only by field ion microscopy (for a review see [16]).

### **Aggregation and pattern formation**

The metastable patterns formed during metal aggregation at low temperature became observable for the first time through the introduction of variable temperature STM. These patterns are model objects ideally suited for diffusion limited aggregation studies. Up to now, there existed only computer models [17, 18] and much more complicated experimental systems like ice [19] and snow crystals [20], fluid systems, i.e., branching of a low-viscous medium during its rapid propagation into one of high viscosity (Saffman-Taylor instability) [21], or the branched growth of bacterial colonies [22].



Interestingly all these non-equilibrium growth processes from physics, chemistry and biology result in patterns which have a conspicuous similarity. Therefore many attempts have been made to discover common mechanisms underlying their growth [23]. The central question in this context is what causes some patterns to be dendritic, as e.g. snowflakes, while others grow randomly ramified. In general the transition from fractal to dendritic growth is explained by dominance of anisotropy over random. In electrochemical deposition this transition is observed for variation of the growth speed [24, 25].

The first metal aggregation experiments, which were carried out for Ag on Pt(111) at low temperature, showed exactly the same transition from dendritic patterns with threefold symmetry to randomly ramified ones upon variation of the deposition rate, i.e., the growth speed [26]. Since metal aggregation on an fcc(111) surface is a well defined and much simpler experimental system than the ones cited above, there was hope that the microscopic mechanism responsible for dendritic growth and that for the transition to random growth could be identified. In fact dendrites were found to be the most common growth patterns for metal aggregation on hexagonal substrates [12, 27]. The mechanism underlying their formation was found to consist in the relaxation of atoms which are one-fold coordinated to the island edge to two-fold coordinated sites. This relaxation is highly asymmetric as could be verified with effective medium theory calculations which I performed in Copenhagen within the group of Prof. J. Nørskov. That this relaxation indeed yields dendrites with trigonal symmetry as observed in the experiments could be verified with kinetic Monte-Carlo simulations which were as well performed in collaboration with Prof. J. Nørskov in Denmark [12].

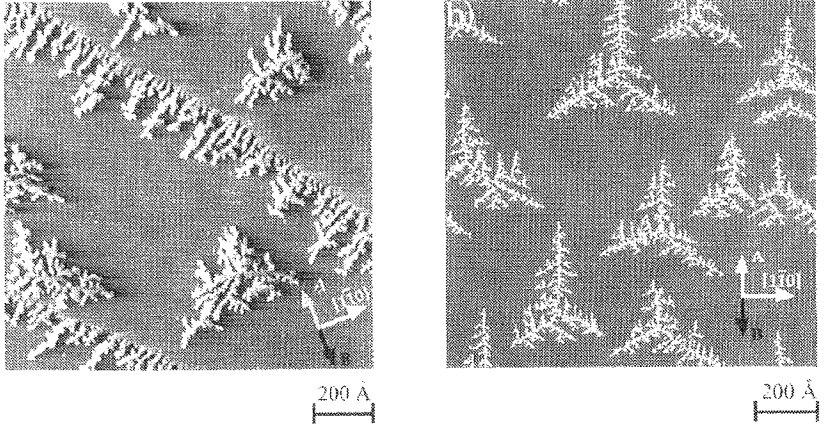


Figure 1. a) STM image of dendritic patterns forming for Ag aggregation on a Pt(111) substrate at 120K. b) Kinetic Monte-Carlo simulation.

The most important result of these studies is that in general, metal aggregation on hexagonal substrates always leads to dendrites with an arm width of at least 2 atoms. This is in contrast to the picture that metal aggregation should be the experimental realization of the simple hit and stick diffusion limited aggregation. At higher temperatures edge diffusion leads to an increasing thickening of the aggregates branches. The arm width was observed to obey an Arrhenius law and barriers for edge diffusion can be extracted from this behavior [28].

Diffusion and sticking anisotropy on fcc(110) substrates can be exploited to grow several hundred atoms long chains which can be as narrow as one atom wide [3, 29]. These first results have been obtained for Cu/Pd(110), recent experiments show that also Pd forms these one-dimensional chains so that the mechanism is not element specific but only due to the specific symmetry of an fcc(110) substrate. The symmetry implies a pronounced diffusion anisotropy which can be extended at low temperature such that diffusion

perpendicular to the close packed rows, which has the higher activation energy, is frozen in. Also the sticking probability is strongly anisotropic. The interactions within the atomic troughs are much stronger than those perpendicular to the close packed rows since the interatomic distance is by a factor of  $\sqrt{2}$  bigger in that direction.

## Outlook

The development of the diffusion controlled growth technique to create large quantities of nanostructures evolved as an immediate consequence of my studies of the atomic diffusion and relaxation processes taking place in metal epitaxy, which have been summarized above. The ability to exploit the laws of nature to create structures of desired morphology in great abundance opens up a new and promising field of research. It is expected that nanostructures obey physical and chemical properties which are quite different from those of the bulk. For instance, it was proposed that small clusters or even single adatoms of Ru, Rh, and Pd, which are elements that are non magnetic in the bulk, should have giant magnetic moments when adsorbed on Ag(001) [30]. The magnetic properties as a function of size and geometry of nanostructures can now be addressed experimentally, e.g., through combination of surface magneto-optical Kerr effect (SMOKE) and variable temperature STM as a structural method. Further interesting questions are the structural dependence of the chemical reactivity or the superconductivity for small aggregates on a crystalline substrate. The general way to address these questions will be to combine an STM or AFM (atomic force microscope) with conventional integrating surface sensitive techniques. In the case of superconductivity, the STM can even serve to detect locally whether an island is in the superconducting state by means of its band gap detectable with scanning tunneling spectroscopy.

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