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# NOVEL FORMATION AND DECAY MECHANISMS OF NANOSTRUCTURES ON THE SURFACE*

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For decades the research on thin-film growth has attracted considerable attention as these kinds of materials have the potential for a new generation of device application. It is known that the nuclei at the initial stage of the islands are more stable than others and certain atoms are inert while others are active. In this paper, by using kinetic Monte Carlo simulations, we will show that, when a surfactant layer is used to mediate the growth, a counter-intuitive fractal-to-compact island shape transition can be induced by increasing deposition flux or decreasing growth temperature. Specifically, we introduce a reaction-limited aggregation (RLA) theory, where the physical process controlling the island shape transition is the shielding effect of adatoms stuck to the stable islands on the incoming adatoms. Moreover, the origin of a transition from triangular to hexagonal and then to inverted triangular as well as the decay characteristics of three-dimensional islands on the surface and relations of our unique predictions with recent experiments will be discussed. Furthermore, we will present a novel idea to make use of the condensation energy of adatoms to control the island evolution along a special direction.

**Keywords:** nanostructures on the surface, formation and decay, kinetic monte carlo simulation, rate equation analysis
**PACC:** 6150C, 6810J, 6822, 6890

## I. INTRODUCTION

Nanoscale structures on the surface are on the focus of exploratory work for next generation devices in the fields of electronic and optical industry, which rely on materials of ever increasing complexity and decreasing size. In most cases these nanostructures must be fabricated through either homoepitaxial or heteroepitaxial growth. The understanding of the kinetics involved in the formation and stability of nanostructures on the surface is of importance for the fast-growing area of nanotechnology. So far, substantial experimental and theoretical studies have been concentrated on the evolution of morphological features on the surface and the growth modes, as well as on the decay of three-dimensional islands. In this paper we will summarize the recent study of the novel formation and decay mechanisms of nanostructures on the surface.

## II. REACTION LIMITED AGGREGATION IN SURFACTANT-MEDIATED EPITAXY

In heteroepitaxial growth the presence of strain often leads to a three-dimensional (3D) growth mode since the equilibrium structure involves strain-relieving effects. A breakthrough was achieved in 1989 when Copel*et al*[1] demonstrated that the use of a single layer of As can improve the heteroepitaxial growth of Ge on Si. This remarkable behavior was termed the "surfactant effect". Since then, a large number of experimental and theoretical efforts have been devoted to the understanding of the surfactant effect.[2] Now, surfactants have been successfully used to modify the growth mode in various systems. However, most of these works concentrate on the mechanism of how surfactants change the growth mode from 3D island to layer-by-layer (LBL) growth,[3−6] while little effort has been made to understand the pattern formation of 2D islands in the early stage of nucleation

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in surfactant-mediated growth.

Recently, the 2D-island pattern formation in epitaxial growth mediated by surfactants was studied in experiments. The effects of a Pb monolayer as a surfactant in Ge growth on the Si(111) substrate were studied systematically by Hwang *et al.*[7] They found a novel nucleation and growth behavior, which clearly contradicts traditional expectations. In these experiments, the 1×1 Pb/Si(111) phase which is an unreconstructed Si substrate is prepared. Each Pb atom saturates a dangling Si atom in the first-layer and the Pb atoms form a complete monolayer. In the growth of Ge islands on this Si(111) surface covered by a Pb monolayer , they found that large fractal islands were formed at low flux or high temperature, while small compact islands were formed at high flux or low temperature. This is contrary to the traditional diffusion-limited aggregation (DLA) theory and the experiments with other systems mentioned above.

A reaction-limited aggregation (RLA) theory was proposed to understand the experimental observations, which includes only three basic energy barriers: one against the diffusion of mobile adatoms on the surfactant terrace, one against the place exchange of mobile adatoms with their underneath surfactant atoms (seeding), and one against the aided place exchange of stuck adatoms with their underneath surfactant atoms.[8,9] It is found that the island shape transition and the island density evolution are controlled by the shielding effect of the stuck adatoms on the mobile adatoms. This effect prevents other incoming adatoms from joining the stable islands through the same sites.

Within the framework of this simple model, a kinetic Monte Carlo (KMC) simulation was used to study the shape transition. KMC simulations have been widely used to study crystal growth. The main idea behind KMC is to describe stochastic processes (such as deposition, diffusion, exchange, desorption, etc.) on the microscopic scale by rates $\Gamma^{(i)} = \Gamma_0^{(i)} \exp(-E_{\rm d}^{(i)}/K_{\rm B}T)$, where $\Gamma_0^{(i)}$ is the effective attempt frequency, $E_{\rm d}^{(i)}$ is the activation energy corresponding to certain process, $K_{\rm B}$ is Boltzmann constant, and $T$ is temperature. In KMC a process $i$ is thermally activated with a relative probability given by $\omega^{(i)} = \Gamma^{(i)} / \sum_i \Gamma^{(i)}$. With these rates, KMC algorithm can easily establish the relationship between KMC time and real time. This can be found in detail in Ref.[10]. KMC differs from the Metropolis Monte Carlo scheme which is used to determine the static properties of the system, and it can describe the real time evolution of the system.

Here, we start with an ideally flat substrate of material $A$ covered with a complete surfactant layer of material $S$. Atoms of material $B$ are deposited onto the surfactant layer at a given deposition rate. We define three types of $B$ atoms: the mobile active adatoms, the stuck active adatoms, and dead adatoms which correspond to the diffusion barrier, the seed exchange barrier, and the aided exchange barrier by $V_{\rm d}$, $V_{\rm se}$, and $V_{\rm ae}$, respectively. Effect of the binding energy $V_{\rm b}$ between adatoms is also investigated. The four barriers satisfy the inequality chain $V_{\rm b} \ll V_{\rm d} < V_{\rm ae} < V_{\rm se}$. The choice of $V_{\rm b}$ has to satisfy the condition that for an adatom with the most of neighbors ($n$=3 on the square lattice and $n$=5 on the triangular lattice), the barrier to detach from an island on the surfactant layer should still be clearly lower than the exchange barrier for the adatom to dive in. $V_{\rm d}$ is the smallest among the remaining three barriers, because adatom diffusion is often significantly enhanced due to the passivation of the surface by the surfactant layer. $V_{\rm se}$ is the largest, making the formation of nucleation centers the most difficult rate-limiting process. Over all, our model is consistent with the fact that the binding energy between $A$ and $B$ is typically much larger than that between $A(B)$ and $S$. The second inequality reflects the fact that there is an effective repulsive wall surrounding the seed atom or an island formed underneath the surfactant layer. The existence of such a repulsive potential to the incoming adatoms due to the presence of the surfactant atoms surrounding an island was proposed previously, and its effect on the island density was investigated recently.[6,11]

The temperature dependence of the island shapes obtained at a deposition rate $F$=0.005 ML/s and coverage $\theta$=0.1ML without binding energy is shown in Figs.1(a) and 1(b). At a low temperature, 300K, compact islands are formed, as shown in Fig.1(a). On the other hand, fractal islands are formed when the temperature is raised by 40K, as shown in Fig.1(b). The transition from compact to fractal patterns takes place at approximately 315K. The flux dependence of the island shapes obtained at $T$=300K and $\theta$=0.1ML is shown in Figs.1(c) and 1(d). Figure 1(c) is an ideal fractal pattern at the flux of 0.0001ML/s, and Fig.1(d) represents an ideal compact pattern at the flux of 0.028ML/s. In the above simulations, we took the energy barriers ($V_{\rm d}$, $V_{\rm ae}$, $V_{\rm se}$)= (0.59eV, 0.82eV, 0.90eV).

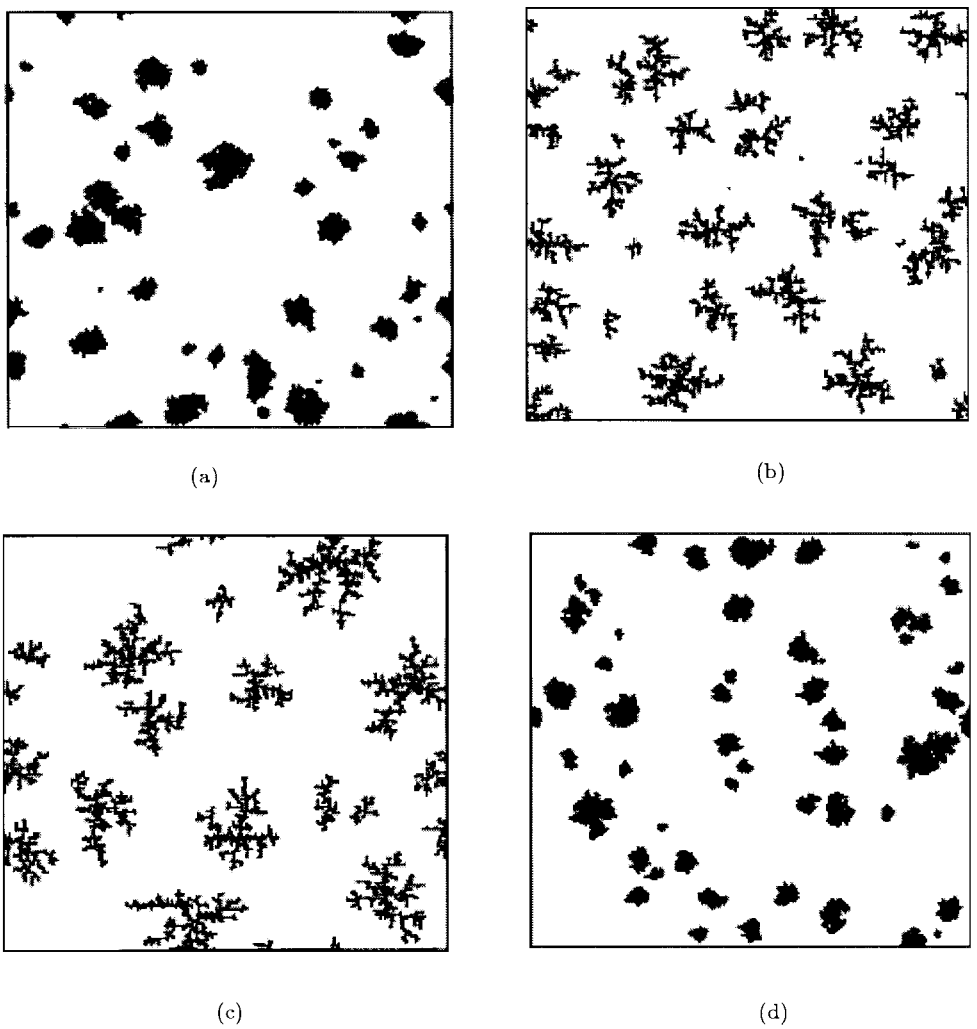



**Fig.1.** Island shape transitions obtained for different temperatures: (a) 300 K and (b) 340 K with a constant deposition flux of 0.005ML/s; and for different fluxes: (c) 0.0001 ML/s and (d) 0.028 ML/s at a constant temperature 300K.

We have expanded the range of applicability of our simple model to various more realistic growth systems in several respects, such as variations of the basic model parameters, consideration of the detachment of the adatoms trapped around the edge of a stable island, and the possibility of simultaneous exchange of multiadatoms as well as a rate equation analysis. None of these improvements change the qualitative fractal-compact transition with the temperature or the flux. In this case, the physical process controlling the island shape transition is the shielding effect of adatoms stuck to stable islands on incoming adatoms.

## Ⅲ. PATTERN ELECTION IN THE PRESENCE OF ADSORBATES

In the earliest stages of Pt(111) homoepitaxy where only single-layer islands are formed, Michely *et al.* found that the islands develop fractal or dendritic shapes at low growth temperatures, but are compact at higher temperatures.[12] In particular, the compact islands can select triangular, hexagonal, and inverted triangular shapes as the growth temperature is increased. This set of observations regarding the shape evolution of the Pt islands has defied a consensus explanation for years, despite many subsequent theoretical and experimental studies. The chance of eventual identification of the missing microscopic mechanisms for the shape evolution was greatly enhanced by the surprising finding of a new experiment, in which the same group attributed the origin of the shape evolu-

tion to the effects of very low concentrations of adsorbed CO in the growth system.[13]

There are two types of close-packed steps on the (111) surface of fcc metals, the (100)-faceted or A-type step with each of its edge atoms having a single nearest neighbor at the base of the step, and the (111)-faceted or B-type step with each atom having two nearest neighbors.[12] These close-packed A- and B-type steps dominate the periphery of the islands on an fcc(111) surface because all other open steps would typically have much higher step formation energies. On considering the redistribution of atoms along the periphery of an epitaxially growing island on fcc(111), three elemental atomic rate processes must be taken into account: (a) edge-to-edge (or simply edge) diffusion with an activation energy $E_{2\to2}$; (b) edge-to-corner diffusion with $E_{2\to1}$; and (c) corner-to-edge diffusion with $E_{1\to2}$. For a given type of step, we generally expect $E_{1\to2} < E_{2\to2} < E_{2\to1}$, because lowering coordinations normally would cost more energy.

For a clean growth, we choose strictly to adopt the activation energies from the only set of data available, i. e. Feibelman's first principles calculations.[14] All islands obtained in a clean growth of Pt/Pt(111) in the temperature range of 450–650K are nearly triangular-shaped with much longer B-type step edges. In particular, there is no shape transition over the whole temperature range studied. These results are in complete qualitative agreement with the recent experimental observations under "clean" growth conditions,[13] and have been obtained for the first time from KMC simulations in which all relevant energy barriers were taken from first principles calculations for the same system of Pt/Pt(111) without any tuning.[14]

For the case of CO-induced growth, the CO preferentially adsorbs at the A-type steps.[15,16] Therefore, decoration of CO at the A-type steps naturally is supposed to weaken the binding strength of a Pt atom at the A step, in particular at or near the lower edges of the step where the upper edges have been blocked by CO molecules. We assume that the decrease of binding energy has a lower limit of $\Delta E_{\mathrm{A,CO}} > 0.1\mathrm{eV}$ in order to cause a reversal in the edge-to-corner rate anisotropy. These simulation results shown in Fig.2 clearly demonstrate the beautiful transitions in the Pt island shapes caused by an increasing concentration of the CO molecules decorating the A steps, provided that the adsorption of CO reverses the intrinsic edge-to-corner rate anisotropy.[17]

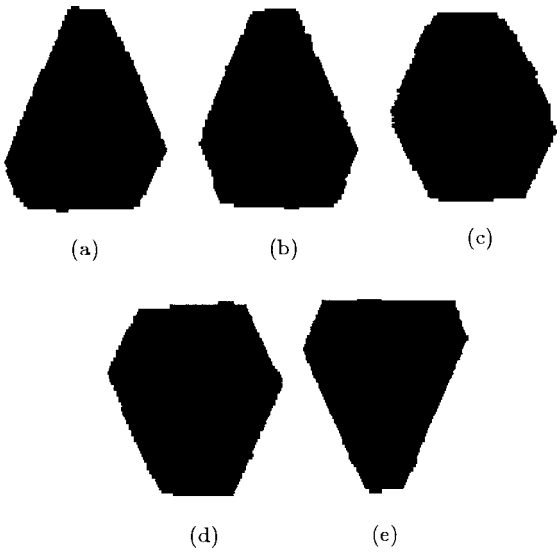



**Fig.2.** CO-induced island shape selection at 500 K. From left to right, the CO concentration $\theta$ at the A-steps is (a) 0.0, (b) 0.01, (c) 0.1, (d) 0.3, and (e) 0.8, respectively.

## IV. ISLAND EVOLUTION CONTROLLED BY CONDENSATION ENERGY

An adatom deposited on a surface will dissipate its latent condensation heat which is of the order of several eV. Such a condensation energy is much higher than the thermal activation energy required for an adatom to diffuse on a surface, which amounts to a few tenths of an eV only. This condensation energy will assist diffusion, namely the transient mobility.[18–21] Our first attempt is to make use of the condensation energy of adatoms to control the island evolution.[22]

Following classical nucleation theory, the flux of the adatoms on the surface attaching to an existing island is obtained. Without considering the contribution of the condensation energy, one would find only compact islands of square shape when frequent edge diffusion and corner crossing take place at higher temperatures. Now, let us consider the contribution of the condensation energy. In this case, the illuminated island edge has more landing atoms than other edges. The experimental evidence supporting the existence of the transient mobility indicates that adatoms on the illuminated edge must have higher mobility to cross the island corner. This anisotropic island corner crossing induces a net current which transfers the adatoms from the illuminated edge to its neighboring edges and may dramatically change the symmetry of the growing island.

We demonstrate that the condensation energy of atoms deposited directly on the illuminated island

edge during epitaxial growth has an important impact on island shape evolution. A small amount (much less than 1%) of energy transfer from the condensation energy into adatom motion induces a net adatom current that transfers adatoms from the illuminated island edge to other island edges and changes the island symmetry. The elongation instability is most pronounced with increasing temperature at a well-defined incident angle.

## V. KINETIC STABILITY OF NANOSTRUCTURES ON THE SURFACE

In order to assess the stability of 3D nanostructures, the nature of the processes responsible for the decay of nanostructures has to be understood and furthermore a precise knowledge of the activation energies involved in the relevant processes is required. Among these, the diffusion of adatoms across step edges is most important because it influences the mass transport between terraces of different heights. A new effective mechanism of interlayer mass transport was proposed in the decay of islands and mounds, which bypasses the Schwoebel-Ehrlich (SE) barrier for the diffusion of atoms over step edges.[23] The channel for rapid mass transport opens when a 2D island engaged in a random walk on a surface touches the boundary of a descending step. Such an edge contact decay channel has significant consequences on the stability of mounds.

Here, we propose two different interlayer mass transport mechanisms to study the stability and decay of 3D nanostructures.[24] One is the multi-site interlayer mass transport mechanism: adatoms can cross a descending step at many sites of the edges of an island. The other is the selective-site interlayer mass transport mechanism: adatoms can cross down to the next layer only at some selective (such as kinked) sites. Such different interlayer mass transport mechanisms will cause different characteristics of 3D island decay. If adatoms on a given layer can cross the descending steps at most sites of the island edges, an optimal island slope and a constant terrace width will be selected during the island decay. However, if adatoms can cross the descending steps only at some limited sites, the island decay will be accompanied by an increase of the island slope. Such interlayer mass transport mechanisms can be used to understand the experimental observations regarding the decay of 3D Cu islands on the Cu(100) and (111) surfaces.[24] Furthermore, these generic conclusions are applicable to the study of the stability and decay of 3D nanostructures in other systems.

The KMC method has been used to study the two interlayer mass transport mechanisms. On the (100) surface, we simulate the decay of a five-layer island with a chosen size of about 6000 atoms on top of a large flat surface. The activation barrier is $V_{\rm ss}$=0.62eV for a straight step process and $V_{\rm ks}$=0.52eV for a kink site process, such that the adatoms are much more likely to descend to the next layer at the selected sites. The predicted time dependence of the size of each layer observed at 400K is shown in Fig.3(b), where 1, 2, 3, 4, and 5 denote the layers of the island from the top layer to the bottom layer, respectively. It is shown that the decay rates of the top and bottom layers are faster than those of other layers. For the middle layers, the additional atoms descending from the upper layer must be received, while, on the other hand, some adatoms descend to the lower layers. Since there is a rough balance in these two processes, the decay rates of the middle layers have no distinct time dependence.

For a (111) surface, the activation energy barriers are chosen as $V_{\rm SS}$=0.43eV and $V_{\rm KS}$=0.40eV. Thus, basically, adatoms can descend from any site along the periphery of the layer. Figure 3(a) shows the island layer size as a function of time at 400K. The number of atoms of each layer also changes linearly with time, but is drastically different from that of the (100) surface with the decay rate of each layer being approximately equal. The difference in the island decay between the two different cases can be explained as follows: Under the any-site channel mechanism, adatoms can descend to the next layer at both straight steps and kink sites. Thus, the perimeter of each layer determines its decay rate. The longer the perimeter of a layer, the more the diffusion channels available. For the middle layers, their next layers provide more diffusion channels. Hence, it can be imagined that their decay rates would be faster than those of the upper layer. However, there are additional adatoms descending to them, slowing down their decay rates. For the bottom layer, the absence of ES barriers and the fast terrace diffusion would make it decay very fast as before. But the perimeter of the bottom layer is much longer than those above, so it provides many more mass transport channels to the adatoms of its upper layer. Thus, more adatoms descend to the bottom layer and slow down the fast decay rate of the bottom layer. The perimeter of each layer becomes longer from the top layer to the bottom. Consequently, each layer provides more dif-

fusion channels to its upper layer. Though adatoms of lower layers have more channels to descend than their upper layers, they have to receive more descending adatoms than their upper layers. Therefore, the decay rate of each layer will tend to be the same. The decay characteristic of 3D islands formed on surfaces is investigated based on different interlayer mass transport mechanisms. If the adatoms on a given layer can descend from any site along the periphery of the layer, an optimal island slope and a constant terrace width will be selected during the decay. In contrast, if the adatoms can descend only through a few selective (such as kinked) sites, the decay will be accompanied by an increase of the island slope. These generic conclusions provide the basis for microscopic understanding of the decay of nanostructures formed experimentally in fcc(111) and fcc(100) metal epitaxy, and are applicable to other systems as well.

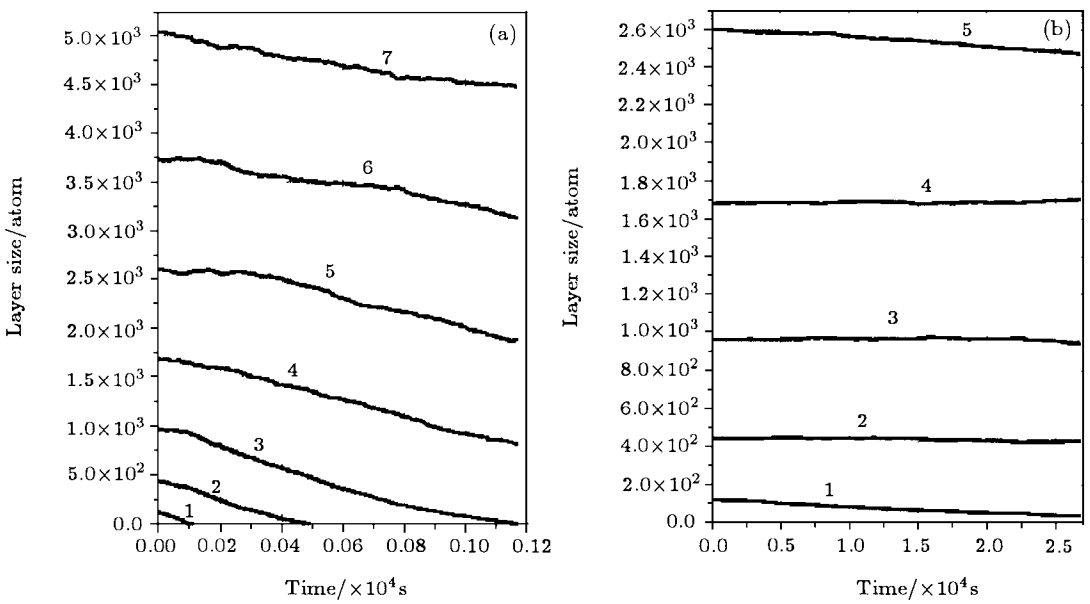



**Fig.3.** The layer-resolved evolution of an island decaying at 400K (a) via the any-site interlayer mass transport mechanism and (b) via the selective-site interlayer mass transport mechanism.

## VI. CONCLUDING REMARKS

The study on the formation and decay mechanisms is very important in the practice of electronic and optoelectronic devices. By scanning tunneling microscopy studies and theoretical modeling, we have uncovered some of the building regulations down to the atomic scale.

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