Formation mechanism of adatom islands on fcc (111) substrates

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Abstract

We explore the effects of various basic atomic processes on the island shapes of diffusion-limited-aggregate growth on a triangular lattice using kinetic Monte Carlo simulation. Edge diffusion and bond-reducing relaxation of double-coordinated adatoms, as well as single-coordinated adatoms, are proved to be essential to the island shape transition from fractal to irregularly compact and from irregularly compact to hexagonal islands, respectively. Shape transitions of adatom islands on fcc (111) substrates can be understood naturally by this model.

1. Introduction

Growth and morphology of crystals are determined by many factors such as growth modes, strain, faceting, etc [1, 2]. It is well known that in epitaxial growth there are three growth modes: Frank–Van der Merwe, Volmer–Weber, and Stranski–Krastanov [1]. Usually, the Frank–Van der Merwe mode is necessary for growing smooth films, but other modes may be useful for growing special structures such as quantum dots. Controlling the early stage in epitaxial growth is very important to the whole growth process and the resultant thin film quality. In order to control the early-stage growth it is necessary to study and understand the microscopic atomic processes and their effects on the nucleation and evolution of adatom islands with respect to various growth parameters. On the other hand, pattern formation of two-dimensional adatom islands on surfaces is also one of the very interesting topics in surface science and statistical physics.

The classic diffusion-limited-aggregation (DLA) theory is the basic framework for understanding the nucleation and evolution of adatom islands in epitaxial growth [3]. It is accepted that fractal islands are achieved in the limit of very little relaxation, for example at low temperature or high adatom flux. In contrast, compact islands are obtained in the regime where atomic relaxation is important, for example at high temperature or low adatom flux [4–9]. In the compact regimes, island shape evolves with growth temperature, deposit flux and other parameters. As a rule, at first some irregularly compact islands are achieved and then they change to regular compact islands, the shape of which is determined by geometry of the substrates [4, 5]. In the limit of zero relaxation, an approaching adatom hits and sticks to an existing island and becomes a member of the island at once. One always observes fractal islands on any substrate. However, with real adatom relaxations taken into account, fractal islands cannot be achieved on typical (100) substrates (or squared lattice), but can be obtained on typical (111) substrates (or triangular lattice) [4, 10] along with the compact islands. The evolution of island density with temperature, adatom flux and other parameters has been established [11] and the formula of adatom island density has been successfully used even to quantitatively describe the epitaxial growth of well known quantum dots [12]. The evolution of Ge islands grown on Si(111) substrates precovered with a complete monolayer Pb as surfactant was explored experimentally [13] and theoretically [14]. The Pt homoepitaxial growth with CO molecules as adsorbates was also studied intensively [15–17]. For these two growth systems, the effects of the Pb surfactant and CO molecules on the island shape transitions were made clear, respectively. On the other hand, the roles of microscopic atomic processes in determining the evolution of adatom island shapes in DLA growth systems are not completely understood [8], although much effort has been made. It is accepted that relaxation of adatoms with one nearest neighbour, or single-coordinated adatoms, plays a key role in making the arms of the fractal islands thicker [8, 10, 11], but it has not been settled which basic atomic process plays the key role in making the island shape change from fractal to compact [8, 11]. In particular, one should answer the question: what basic atomic processes are responsible for determining the shape transitions of various compact islands?

In this paper we explore the effects of various basic microscopic atomic processes on the adatom island shapes in epitaxial growth on fcc (111) substrates using kinetic Monte Carlo (KMC) simulation. Here by ‘basic microscopic atomic process’ we mean that an adatom at most moves onto one of its nearest neighbouring sites in a single simulation
step. This implies that we do not consider composite atomic processes such as corner-dependent processes [8–10], where an adatom should move beyond its nearest neighbouring sites. We consider four basic adatom atomic processes, namely relaxation of a single-coordinated adatom into an $n$-coordinated adatom ($P_{1n}$, always with $n \geq 1$) and relaxation of a double-coordinated adatom into an $m$-coordinated adatom ($P_{2m}$ with $m \geq 2$), relaxation of a double-coordinated adatom into a single-coordinated adatom ($P_{21}$), and detachment of a single-coordinated adatom from the islands they belong to ($P_{10}$). Any adatom with three or more nearest neighbours is considered to be inactive; it cannot move because its energy barriers are much higher than those of single-coordinated and double-coordinated adatoms. Besides the known conclusion that the $P_{1n}$ processes make the fractal arms thicker [8, 10], we further obtain that $P_{2m}$ with $P_{1n}$ is enough to make the islands change from randomly fractal to irregularly compact in shape; $P_{21}$ is responsible for the transition from the irregularly compact to hexagonal compact islands; $P_{10}$ makes the islands become bigger and more regular. Real shape evolution of adatom islands, with growth temperature or adatom flux, on fcc (111) substrates can be naturally understood in the framework of this model.

In the next section we shall introduce the basic atomic processes and explore their effect on the adatom island shape. In section 3 we shall present the evolution of adatom islands with the temperature and flux, emphasizing the island shape transition from fractal to irregularly compact and further to regular compact. Finally, we shall present a discussion and a summary in section 4.

2. Basic atomic processes and their effect on island shape

We begin with a flat triangular lattice which describes fcc (111) substrates in our KMC simulation. Adatoms are randomly deposited on the lattice at a flux $F$. A free adatom without any nearest neighbour can hop onto the lattice with a rate $R_{\text{diff}} = v_0 \exp(-V_{\text{diff}}/kT)$, where $v_0$ is the attempt frequency, $V_{\text{diff}}$ is the free diffusion barrier, $k$ is the Boltzmann constant, and $T$ is the growth temperature. The two relaxation processes, $P_{1n}$ and $P_{2m}$, correspond to the two barriers $V_{1n}$ and $V_{2m}$, the bond-reducing process, $P_{21}$, has barrier $V_{21}$, and the detachment process, $P_{10}$, of single-coordinated adatoms corresponds to the barrier $V_{10}$. The four basic processes are demonstrated in figure 1. For convenience we define the relative barriers: $\Delta V_{1n}$, $\Delta V_{2m}$, $\Delta V_{21}$, and $\Delta V_{10}$ so that $V_{1n} = V_{\text{diff}} + \Delta V_{1n}$, $V_{2m} = V_{\text{diff}} + \Delta V_{2m}$, $V_{21} = V_{\text{diff}} + \Delta V_{21}$, and $V_{10} = V_{\text{diff}} + \Delta V_{10}$. Any adatom with more than two neighbours is considered to be inactive, but an inactive adatom may become active with its neighbourhood changing in the presence of the processes $P_{21}$ and $P_{10}$. The inequalities $V_{1n} < V_{21} < V_{10}$ and $V_{2m} < V_{21} < V_{10}$ are reasonable at least for most real epitaxial growth systems on fcc (111) substrates, but we shall from time to time go out of this parameter regime to clearly demonstrate special roles of different atomic processes in the following KMC simulations.

In the limit of the ideal DLA hit-and-stick regime, a free adatom can hop from site to site with the rate $R_{\text{diff}}$, all the relaxation processes at the island edges are switched off, and there is no relaxation for any adatom, therefore one obtains ideal fractal islands. Nevertheless, in real growth systems there are always relaxations for some adatoms or most adatoms. This means that some or all of the four basic edge processes are active in real growth systems. At first, in order to understand the role of one single process of the above four, we switch on only one of the four processes in addition to the free diffusion in every simulation. We find that any process alone cannot change the island shape substantially, so the islands are still fractal. The process $P_{2m}$ or $P_{21}$ alone has very little effect on the island shape, but $P_{1n}$ or $P_{10}$ alone can make the fractal arms thicker. In fact, even $P_{2m}$ and $P_{21}$ together change the island shape very little, as figure 2(a) shows. $P_{1n}$ and $P_{10}$ together substantially increase the width of the fractal arms of the islands (figure 2(b)), but are still not effective enough to make the fractal islands become compact. In order to find the key atom processes which are essential for the shape transition from fractal to compact islands, we make many simulations with various atom edge processes active and at the same time with other processes switched off. It is found that the fractal-to-compact shape transition can be achieved only when both single-coordinated adatoms and double-coordinated adatoms are allowed to move. A typical result with $P_{1n}$ and $P_{2m}$ switched on is shown in figure 2(c), in which the two atom processes achieve the shape transition to the irregularly compact islands. For comparison the KMC simulations are carried out, keeping $P_{10}$ and $P_{2m}$, or $P_{1n}$ and $P_{21}$, active. The island shape in the case of $P_{10}$ and $P_{2m}$ is similar to that shown in figure 2(c). This means that $P_{10}$ plays a similar role as $P_{1n}$ in inducing the irregularly compact islands from the fractal islands. The islands in the case of $P_{1n}$ and $P_{21}$ are actually still fractal although the fractal arms have already become much thicker than those in figures 2(a) and (b). Compared with the islands in figure 2(c), it is clear that $P_{21}$ cannot make the adatom substantially relax along the island edges, and therefore it cannot drive the growth system into the compact regime. Further switching on the bond-reducing process, we obtain regular hexagonal compact islands, as shown in figure 2(d). Therefore, we find two shape transitions of the adatom islands in the DLA growth: one is from fractal to irregularly compact islands; the other is from irregularly compact to regular hexagonal islands; these have been observed in some growth systems [5].

Why is it that the edge processes of single-coordinated adatoms alone, or the edge processes of double-coordinated adatoms alone, cannot change the island shape? For a fractal island, the processes $P_{1n}$ and $P_{10}$ can reduce the number of single-coordinated adatoms at the island edges and thereby enhance the fractal arms of the islands, but they alone cannot make adatoms effectively move along the island edges. As a result, these processes, even together, cannot change the island shape. Indeed, $P_{2m}$ and $P_{21}$ can make adatoms move along the straight edges, but there are very few straight edges and very few double-coordinated adatoms for fractal islands, so the effective transport of the adatoms along the island edges cannot be substantially achieved, therefore the islands remain fractal. The adatom transport along the island edges is achieved only when one or both of $P_{10}$ and $P_{1n}$ and one or both of $P_{2m}$ and $P_{21}$ are switched on at the same time. Therefore, the fractal-to-compact shape transition is achieved with the two kinds of adatom processes together switched on.
Adatom islands on fcc (111) substrates

Figure 1. Demonstration of the elementary processes: (a) relaxation of a single-coordinated (SC) adatom ($P_{1n}$); (b) relaxation of a double-coordinated (DC) adatom ($P_{2m}$); (c) bond-reducing relaxation of a DC adatom into a SC adatom ($P_{21}$); (d) detachment of a SC adatom from the island ($P_{10}$). The big open circles represent the atoms that will move, the small open circles are possible sites the atoms will occupy after the corresponding processes take place.

Figure 2. Island shapes for four sets of various switched-on elementary processes: (a) $\Delta V_{1n} = 0.02$ eV and $\Delta V_{21} = 0.07$ eV; (b) $\Delta V_{1n} = 0.01$ eV and $\Delta V_{10} = 0.08$ eV; (c) $\Delta V_{2m} = 0.01$ eV and $\Delta V_{2m} = 0.02$ eV; (d) $\Delta V_{1n} = 0.01$ eV, $\Delta V_{2m} = 0.02$ eV and $\Delta V_{21} = 0.07$ eV. The temperature is 350 K, the diffusion barrier 0.47 eV, the flux 0.08 ML s$^{-1}$, and the coverage 0.1 ML.

Why are there two kinds of compact islands in the DLA growth on fcc (111) substrates? Since the process $P_{21}$ induces the transition from irregularly compact to regular hexagonal islands, it must be the key in understanding the two kinds of shapes and the shape transition. Without the process $P_{21}$, some higher coordinated sites, once formed, will become nucleation centres at the edges so that other adatoms will be absorbed toward them. Because the sites are randomly formed along the island edges, the islands tend to be irregular in shape, although they are already compact. With the process $P_{21}$
switched on, the probability of forming the higher coordinated sites is very small, so that the island shape is determined completely by the geometry of the substrates. On the other hand, the process $P_{21}$ with $P_{1n}$ allows adatoms to cross the island corners, further enhancing the adatom transport along the whole island edge in addition to the direct edge process $P_{2m}$. Therefore, we obtain the hexagonal islands on the fcc (111) substrates with $P_{21}$ switched on, because the substantial adatom transport along the island edges is easily achieved. However, this does not mean that the irregularly compact islands in figure 2(c) can be observed in most real growth systems. In fact, the process $P_{21}$ and others always exist in real growth systems, although they may be small, or very small, so that the irregularly compact islands such as those shown in figures 3 and 4 are frequently observed in real growth systems.
3. Evolution of island shape with temperature and flux

For a given real DLA growth system the energy barriers are already fixed, therefore one can change the growth temperature, the adatom flux, and coverage only. Since the island shape cannot be induced by varying the coverage, we shall explore only the effect of growth temperature and flux on the evolution of island shape. In figure 3 we show the evolution of island shape with the deposition flux rate: (a) \( F = 0.8 \text{ MI s}^{-1} \); (b) \( F = 0.1 \text{ MI s}^{-1} \); (c) \( F = 0.0009 \text{ MI s}^{-1} \); (d) \( F = 0.00005 \text{ MI s}^{-1} \). The growth temperature and the coverage are taken as 300 K and 0.1 MI, the energy barrier of diffusion on the terrace is taken as \( V_{	ext{diff}} = 0.47 \text{ eV} \), a typical value for a metal DLA growth, and the additional barriers are set to be \((\Delta V_{	ext{in}}, \Delta V_{	ext{m2}}, \Delta V_{	ext{m3}}, \Delta V_{	ext{f10}}) = (0.15, 0.16, 0.18, 0.20) \text{ eV}\). The inequalities \( \Delta V_{	ext{m3}} < \Delta V_{	ext{f10}} \) and \( \Delta V_{	ext{m2}} < \Delta V_{	ext{f10}} \) are kept, but the values of the barriers are determined such that various island shapes can be achieved with the same barrier parameters. For most real growth systems energy barriers satisfy these inequalities, but it should be pointed out that there are indeed some exceptions. In figure 3(a) we obtain small fractal islands at the flux \( F = 0.8 \text{ MI s}^{-1} \). The smallness of the islands results from the activation of the detachment process \((V_{	ext{f10}} = 0.47 + 0.20 = 0.67 \text{ eV})\). When the flux becomes 0.1 MI s\(^{-1}\), the islands are still fractal, but their fractal arms become thicker and the island density becomes smaller, as figure 3(b) shows. For smaller flux, 0.0009 MI s\(^{-1}\) in figure 3(c), the islands already become compact, but their shape is irregular. On the other hand, the island density decreases further. When the flux reaches \( F = 0.00005 \text{ MI s}^{-1} \), the island density becomes even smaller and the regular hexagonal islands are obtained. Therefore, the flux induces two shape transitions: fractal-to-compact and irregular-to-regular islands. The former transition is already well known for DLA growth systems, but the latter transition has yet to be emphasized. Anyway, it should be achieved at least in some growth systems because our parameters are typical for DLA growth.

Now we explore the evolution of the island shape with the growth temperature. We keep all the energy barriers unchanged and vary the growth temperature. In figure 4 we show the simulation results with: (a) \( T = 250 \text{ K} \); (b) \( T = 290 \text{ K} \); (c) \( T = 330 \text{ K} \); (d) \( T = 490 \text{ K} \). For the simulations the flux rate is \( F = 0.08 \text{ MI s}^{-1} \) and the coverage is \( \theta = 0.1 \text{ MI} \). At low temperature (250 K in figure 4(a)) we obtain small fractal islands too, but the arms of the fractal islands become thicker at higher temperatures. In figure 4(b) we obtain compacted fractal islands at \( T = 290 \text{ K} \), but when the temperature increases further we should see the fractal-to-compact shape transition. In figure 4(c) the compact islands at \( T = 330 \text{ K} \) are shown, although they are irregular. Finally, at \( T = 490 \text{ K} \) we obtain the regular hexagonal islands, as shown in figure 4(d). There is a compact shape transition from irregularly compact islands to regular hexagonal islands. Therefore, the growth temperature induces two shape transitions as does the flux rate (figure 3). The growth temperature and the flux rate induce the island shape transition with a similar mechanism, as they do for the fractal-to-compact shape transition.

4. Discussion and summary

In our exploration of the flux and temperature dependence of the island shapes, we have varied the barriers of the basic atom processes on quite a large scale. The two shape transitions are clearly obtained for various barrier parameters. This means that the main results we have achieved are general and can be applied to most DLA growth systems. However, the parameter windows in which a given kind of island appears vary in width. Some kinds of islands can be obtained in a wide parameter region, some only in a narrower region, and in special cases some kinds of islands do not appear at all. Actually in experiments the evolution of island shapes varies for different real growth systems because the energy barriers of the four basic atomic processes take different values in different growth systems. In some cases the inequality \( V_{	ext{f10}} > V_{	ext{m3}} \) is not satisfied so that the islands change directly from fractal to a regular compact shape, but in most cases it is satisfied so that the irregularly compact islands can be observed.

In summary, we have explored the effects of the various basic microscopic atomic processes on the adatom island shapes using KMC simulation. We consider four basic adatom atomic processes, namely relaxation of single-coordinated and double-coordinated adatoms (\( P_{\text{m5}} \) and \( P_{\text{m6}} \)), the bond-reducing relaxation of double-coordinated adatoms into single-coordinated adatoms (\( P_{\text{b1}} \)), and detachment of single-coordinated adatoms from the islands they belong to (\( P_{\text{b10}} \)). Besides the known conclusions, we find that \( P_{\text{m6}} \) with \( P_{\text{b10}} \) is enough to make the islands change from randomly fractal to irregularly compact in shape; \( P_{\text{b1}} \) is responsible for the transition from irregularly compact to hexagonal compact islands; \( P_{\text{b10}} \) makes the islands become much bigger and regular hexagons. Real shape evolution of adatom islands, with growth temperature or adatom flux, on fcc (111) substrates can be naturally understood in the framework of this model.

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References


