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Aggregation on heterogeneous surface*

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Chessboard-like substrates are introduced in this paper, in order to study the diffusion-limited aggregation (DLA) and the motion of poly-atoms on heterogeneous surfaces. The effect of morphology of such substrates upon the cluster aggregation is investigated using the Monte Carlo simulation. It is found that the growth process and the cluster morphology are governed by the energetic topography of the substrates. Our simulation also indicate that the island density and the fractal dimension of the clusters depend strongly on the substrate topography and the activation energy.

Keywords: heterogeneous substrate, DLA model, fractal, Monte Carlo simulation
PACC: 0540

1. Introduction

The diffusion-limited aggregation (DLA) mode[1] is one of the most striking examples in computer simulations. It has become important for describing various physical, chemical, and biological phenomena. In particular, it has been successfully used in simulating a broad range of nonequilibrium growth and aggregation processes. The diffusion and aggregation of adatoms on a solid or metal substrate is a fundamental problem in surface science that has attracted attention over many years, and the same is the case for its computer simulation. Many interesting and useful results have been obtained, such as simulation of fractal growth of thin films, the nonlinear behaviour of multiple cluster growth, island morphology and size distribution in submonolayer epitaxial growth, and so on.[2−8] But works about surface heterogeneities constitute only a small proportion. It is obvious that even single crystal surfaces are not perfect and contain structural and electronic heterogeneities because of a large number of contributing factors that can be sorted into two different classes: geometrical heterogeneity (cracks, pits, vacancies, etc) and chemical heterogeneity (impurities, substitutional atoms, etc). These heterogeneities may introduce a complex spatial dependence of the solid–gas interaction potential, which can be denoted as adsorption energy topography.[7] As a consequence, simulations on various kinds of substrates is very important and useful. The influence of surface heterogeneity on the formation of diffusion-limited aggregates is obvious. Large-scale square-lattice DLA clusters indicated that the underlying lattice may affect the asymptotic behaviour of aggregates.[8,9] Recently, some results suggest that during the process of aggregation there is a competition between anisotropy provided by the lattice and randomness due to the stochastic motion of the particles coming to a cluster far from the seed.[8] A theoretical model for reaction-limited aggregation (RLA) is used successfully to study the effect of a monolayer of surfactant on the formation of two-dimensional islands in heteroepitaxial and homoepitaxial growth.[10,11] But in this paper we focus on the influence of topography and surface energetic heterogeneity of substrate without surfactant on the main features of fractal aggregates. The description of thermodynamic phenomena taking place on a substrate which presents the inherent complexity of energetic heterogeneities is a challenging topic in modern surface science. Despite their importance, however, reliable measurements of surface diffusion coefficients are rare, especially for semiconductor surfaces. We attempt to discuss the effects of strong correlated heterogeneities on several surface processes.

The present paper is organized as follows. The ba-

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sic definitions and explanations of the details of models are introduced in Section 2. In Section 3, the simulation methods and the results are presented. Finally, in Section 4, we give conclusions and discussion of the topological properties of a fractal structure.

2. Computer model and basic definitions

Though a complete theoretical understanding of DLA model has not yet been achieved, the algorithm is rather simple. Consider a lattice in two dimensions. The sites of the lattice are either occupied or unoccupied. Growth begins with a seed particle in the centre. We release a random walker far from the centre. The walker moves over the lattice in a stepwise fashion, executing an unbiased random walk. If the random walker moves too far from the growing cluster, it is terminated and a new random walker is started. If the random walker eventually reaches a site that is the nearest neighbour to a previously occupied site, the random walk is stopped and the unoccupied perimeter site is filled to represent the growth process. Useful discussions about the influence of the chessboard-like heterogeneous surface on the formation of diffusion-limited aggregates have been given.[7]

In this paper we continue to discuss the influence of adsorption energy topography, especially on a triangular substrate, and focus on nucleation and island growth based on a kinetic Monte Carlo simulation model, which succeeds in simulating the initial stage of thin film growth. The model is described as follows: atoms are deposited onto a 360×360 chessboard-like heterogeneous surface one by one with an interarrival time Δt, which is related to the deposition flux R and the surface diffusion rate ν. In this paper, we set the unit of Δt to be a diffusion step. This means that when the previous adatom diffuses Δt steps, the next atom is deposited. When the mobile atoms diffuse to their nearest-neighbour sites, they will stick with a unit probability and then a stable nucleus forms. And when the diffusing particles meet the growing cluster or nucleus, it will stick to them and become a part of them.[5]

The chessboard-like heterogeneous surface formed by only two kinds of square patches has been described by Nazzarro *et al.*[7] Here, we introduce another substrate of complex structure which is called chessboard II substrate and shown in Fig.1. The chessboard II substrate is created by placing deep or shallow dots onto the adsorption lattice, and particles can only hop from one dot to another, or stop when it attaches to another. Every deep site has the same attraction energy as the shallow one. Here, we have assumed, without losing generality, that the saddle point energy remains constant throughout the whole lattice. The periodic length is set to $T_L = L_1 + L_2$, where L_1 and L_2 are the unit length of the deep site and the shallow sites respectively. In Fig.1(a), the structure of substrate is similar to the surface structure of GaAs.[12,13]

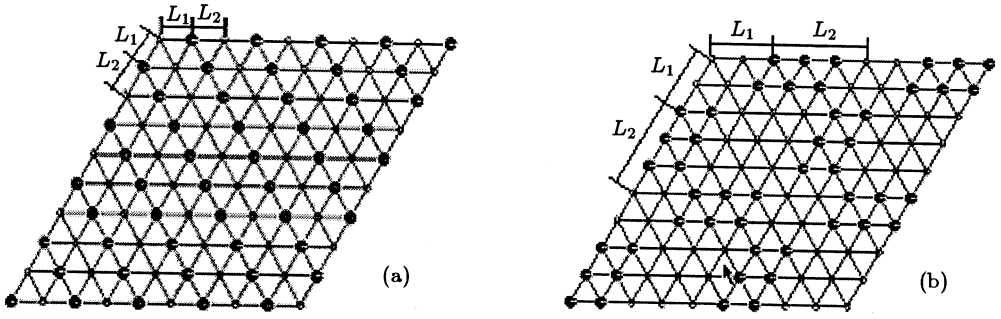


Fig.1. Samples of the chessboard II triangular substrate formed by only two kinds of sites. The attraction energy on the deep site is E_d, and on the shallow site is E_s. The substrate size used here is L=10. (a) L_1=1, L_2=1, T_L=2, L=10, (b) L_1=2, L_2=3, T_L=5, L=10.

The walk of the particle in this lattice is a biased random walk. The associated jump probability of a diffusion particle hopping from the initial site to the final site is given by

$$W_{ij} = \frac{1}{k}\exp(-E/k_B T), \qquad (1)$$

where k is the normalization factor, and E, the activation energy for such jumps, is taken as the energy difference between the final and the initial site energies. k_B is the Boltzmann constant, and T is the substrate temperature. When the particle hops from a deep dot to a shallow dot, the difference of the activation energy is $E_s - E_d$. So the probability of a diffusion particle

hopping from a deep site to a shallow site is described as

$$W_{\rm sd} = \frac{1}{k}\exp(-(E_{\rm s} - E_{\rm d})/k_{\rm B}T). \qquad (2)$$

For simplicity, we use the absolute value of $\Delta E \equiv |E_{\rm s} - E_{\rm d}|/k_{\rm B}T$ in our simulations, and the periodic boundary condition is set up.

3. Computational simulation and results

Eight simulation images are shown in Fig.2, where the simulation condition is set to L=360, ΔE=2, simulated on a triangular lattice. The seed particle is on the centre of the triangular lattice. A single particle is introduced one at a time at a randomly chosen point on the outer circular boundary which is R (=30 units) apart from the outer periphery site. Figures 2(a)–(h) show the evolution of the feature of DLA-cluster upon increasing the value of T_L for fixed ΔE (=2). Figure 2 (a) demonstrates that for small patches the influence of heterogeneous substrate is so faint that we almost cannot distinguish it from the classical DLA cluster grown on homogeneous substrate. As the size of the patch is increased, the morphology of the cluster varies. The feature of the cluster is affected by the energetic topography of the bivariate trap surface obviously. For T_L=4, we find that the feature of cluster is transformed. The DLA-cluster grown on heterogeneous square substrate has been discussed in detail in the literature.[7] So in this paper we focus on cluster grown on the triangular lattice.

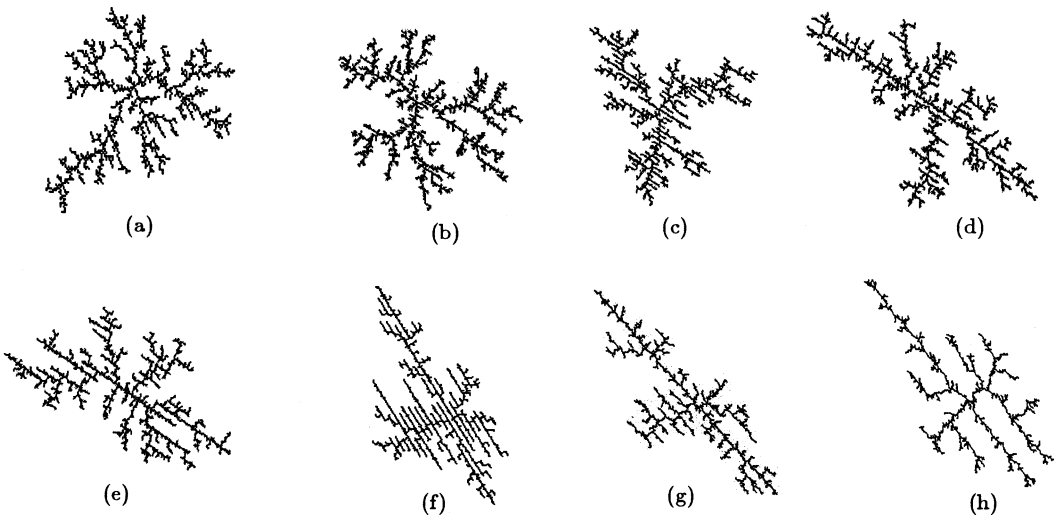


Fig.2. Snapshot of a DLA structure grown on a heterogeneous substrate with (a) L_1=1, L_2=1, T_L=2, (b) L_1=1, L_2=2, T_L=3, (c) L_1=2, L_2=2, T_L=4, (d) L_1=2, L_2=3, T_L=5, (e) L_1=3, L_2=3, T_L=6, (f) L_1=7, L_2=8, T_L=15, (g) L_1=15, L_2=15, T_L=30, (h) L_1=20, L_2=20, T_L=40, where ΔE=2.

Figures 3(a)–(h) show the evolution of the feature of DLA-cluster upon increasing the value of ΔE for fixed T_L. The simulation condition is set to L=360, L_1=7, L_2=8, T_L=15, simulated on triangular lattice. For ΔE=0.5, the cluster grown on chessboard II substrate is similar to the classical DLA cluster grown a homogeneous substrate. This means that the influence of the topography of the substrate is not obvious under this circumstance. But as the value of ΔE is increased, the structure of cluster changes strongly and the number of arms of a cluster decreases. The cluster is stretched along the diagonal direction. When ΔE >3.0, the cluster is changed into a rough stick. The process of transformation of cluster is very important and interesting.

Figure 4 shows multiple clusters grown by kinetic Monte Carlo simulation model on various heterogeneous substrates. The simulation condition is set to L_1=7, L_2=8, T_L=15, L=360, Δt=8000, n=8000. Figures 4(a)–(c) are simulated on square lattice while (d)–(f) are on triangular lattice. It is obvious that the shapes of islands are affected by the energetic topographies of substrates. As the value of ΔE is increased, the island number increases and the arms of clusters become more diluted. The structure of clusters grown on square lattice is different from that on triangular lattice.

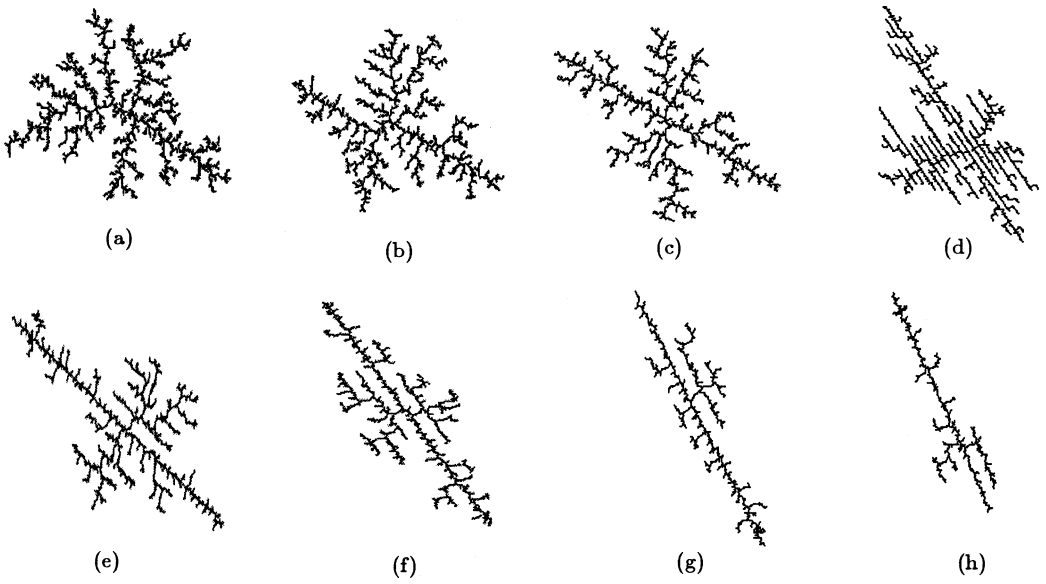


Fig.3. Snapshot of a DLA structure grown on a heterogeneous substrate with (a) ΔE=0.5, (b) ΔE=1.0, (c) ΔE=1.5, (d) ΔE =2.0, (e) ΔE=2.5, (f) ΔE=3.0, (g) ΔE=3.5, (h) ΔE=4.0, where L_1=7, L_2=8, T_L=15.

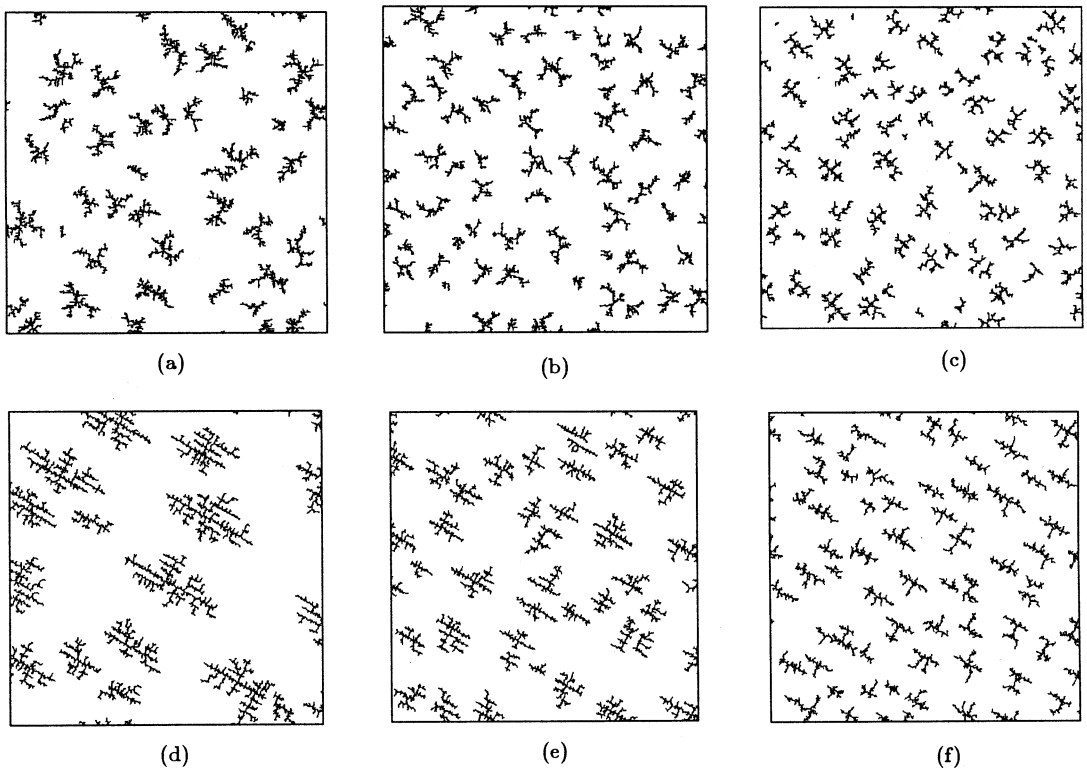


Fig.4. Six simulation results showing the evolution of the island shape and number upon increasing the value of ΔE with (a) ΔE=1, square lattice, (b)ΔE=2, square lattice, (c) ΔE=3, square lattice, (d) ΔE=1, triangular lattice, (e) ΔE=2, triangular lattice, (f) ΔE=3, triangular lattice, where L_1=7, L_2=8, T_L=15, L=360, Δt=8000, n=8000.

Figure 5 shows clusters obtained for different values of T_L. From a simple inspection of the figure, it can be concluded that island shape varies as the size of T_L is increased. But the island number is affected weakly by the value of T_L. As the size of T_L increases the clusters are modified. The main features of the clusters are governed by the structure of the substrate.

In order to study the relationship between island number and ΔE, a series of simulations are performed

for different substrates. All results are shown in Fig.6. We find the number of island grown on square lattice is a constant for fixed T_L=2 (L_1=1, L_2=1) as the value of ΔE is increased. But the number of islands grown on triangular substrate increases weakly. The number of island grown on triangular substrate is smaller than the number of island grown on square lattice under the same condition, and the tendency of increase is similar.

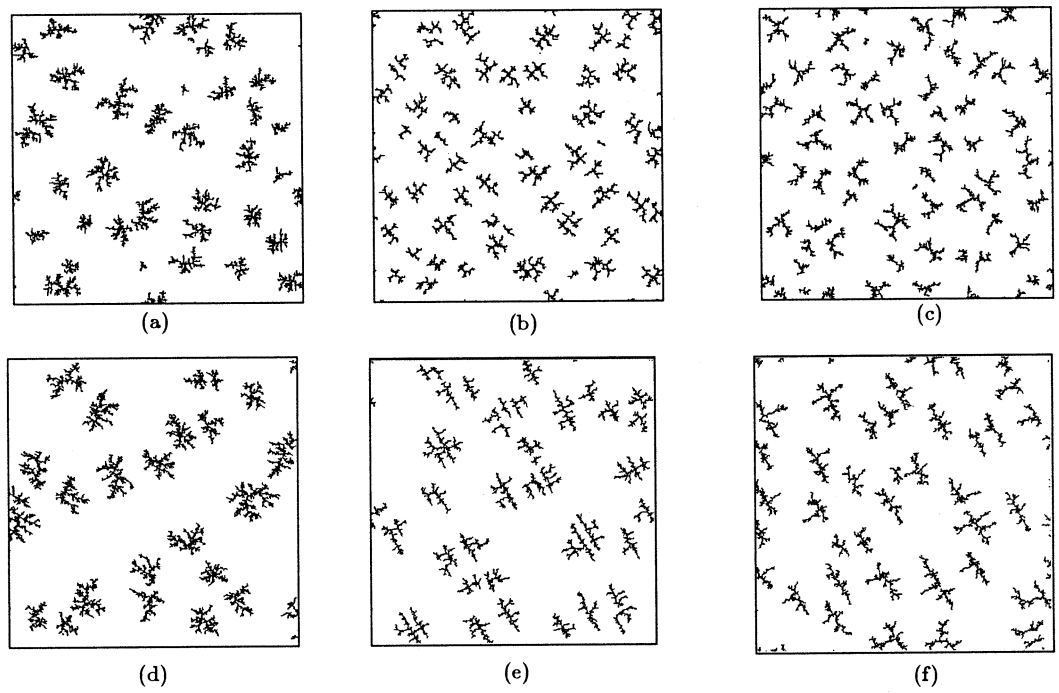


Fig.5. Six simulation results showing the evolution of the island shape and number as the value of T_L increasing with (a) L_1=1, L_2=1, T_L=2, square lattice, (b) L_1=7, L_2=8, T_L=15, square lattice, (c) L_1=15, L_2=15, T_L=30, square lattice, (d) L_1=1, L_2=1, T_L =2, triangular lattice, (e) L_1=7, L_2=8, T_L =15, triangular lattice, (f) L_1=15, L_2=15, T_L =30, triangular lattice, where ΔE=2, L=360, Δt=8000, n=8000.

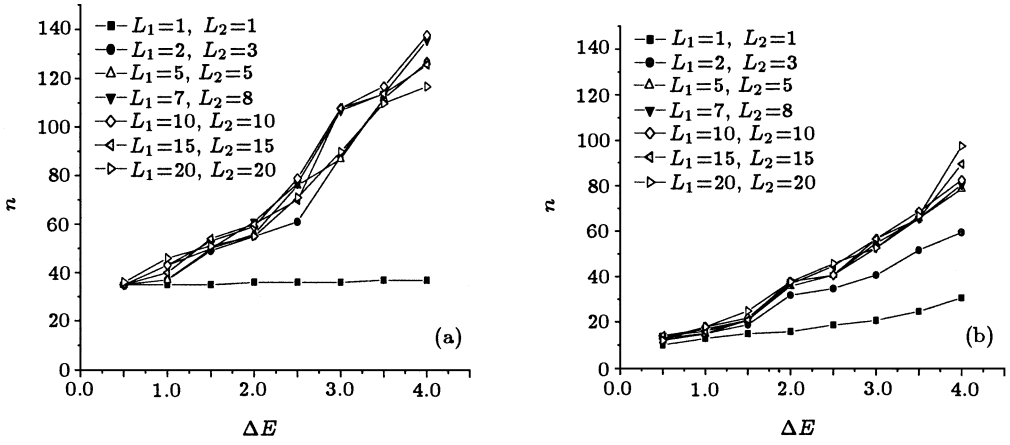


Fig.6. (a) Island number n for variousΔEon square lattice, (b) Island number n for variousΔE on triangular lattice.

We continue to calculate the fractal dimension (d_f) of clusters grown on various heterogeneous substrates. All results are shown in Fig.7. The fractal dimension is almost a constant for different T_L, but it decreases when the value of ΔE is increased. The difference of influence on fractal dimension between triangular lattice substrate and square lattice substrate is faint. This means that the fractal dimension is independent of the surface topology which is similar to the results in Nazzarro's paper.[7]

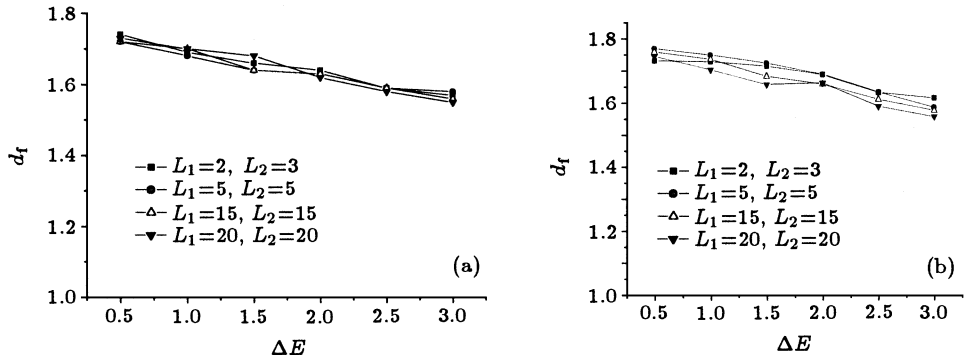


Fig.7. Fractal dimension d_f for various ΔE with (a)L=360, Δt=8000, n=8000, triangular lattice, (b) L=360, Δt=8000, n=8000, square lattice.

4. Conclusion and discussion

In this paper the diffusion-limited aggregation and the motion of poly-atoms on heterogeneous surfaces are studied. From the above simulation results, we can derive some useful conclusions about how the surface topography affects the formation of aggregates.

Two parameters, patch size and adsorptive energy, play important roles in controlling features of the cluster. The patch size controls the main frame of the cluster and the value of adsorptive energy controls the fractal dimension and island number. The larger the patch size and adsorptive energy, the larger the influence of substrate structure on feature of cluster.

From a simple inspection of clusters grown on surfaces with different values of T_L (shown in Fig.2, Fig.4 and Fig.7), it can be concluded that the aggregates present different structures upon increasing the patch size. The arms of clusters are diluted and the main structures are governed by the topographies of substrates as the value of ΔE is large enough. But the island number and fractal dimension are affected weakly. The features of clusters simulated on triangular lattice are different from that simulated on square lattice. The reason is that the neighbour relationship of the triangular lattice is different from that of the square lattice.

When the energy difference between shallow and deep sites is small, the influence of structure of substrate on feature of cluster is faint. As $\Delta E \to 0$, our model becomes the standard DLA model on the homogeneous substrate proposed by Meakin.[8] But as the value of ΔE is increased, the structure of aggregation is controlled by topography of the substrate obviously, and the cluster is stretched along the diagonal direction. When ΔE >3.0, the cluster is changed into a rough stick. The reason is that particles are easy to aggregate in some place with low surface energy. The phenomenon is similar to step flow.[3] In our model, shallow sites have low surface energy which are arranged in a chessboard-like ordered substrate. This gives an inducement to aggregate around the diagonal direction. The island number increases as the value of ΔE increases except for the especial situation L_1=1 and L_2=1. When L_1=1 and L_2=1, the number of islands grown on square lattice remains constant for various ΔE and the number of islands grown on triangular substrate increases weakly. The difference between the square lattice and triangular substrate is produced by the neighbour conditions. We can explain this phenomenon as follows. Adtoms can easily move to shallow sites with low surface energy firstly, but when some shallow sites are occupied, the surface energy of their nearest neighbours, deep sites and shallow sites, become low, and these deep sites become easy to be attached. So the difference between shallow sites and deep sites is diluted. But when $L_1 \geq 2$ and $L_2 \geq 2$, the difference becomes obvious for the separated patch is large enough. The number of islands is mainly controlled by ΔE; because in our model of square lattice, two kinds of sites are separated and cannot be connected; as the value of ΔE is increased, the adatoms cannot walk freely from one site to another site far away. They are governed by Eq.(1) and walk in the patch with low surface energy until another atom deposits and meets it. But on the triangular lattice the two kinds of sites are not separated completely; there are some roads connecting one patch with another. This difference makes the speed of increase of island number different. In particular, when T_L=2 (L_1=1 and L_2=1), the island number is a constant on the square lattice but increases weakly on the triangular lattice (see Fig.6). Though the topography of the sub-

strate affects the structure of aggregation strongly, it affects the number of islands weakly. From Fig.7, it can be concluded that the fractal dimension are not affected strongly by the topography of substrate. But as the value of ΔE is increased, the arms of clusters are diluted and the fractal dimension d_{f} decreases weakly, because when the value of ΔE is increased, the particles cannot walk freely. They can only walk in the patches with lower surface energy. The structures of the clusters are completely governed by the structure of substrate.

In this paper, we investigate the effect of the energetic topography upon the aggregation using the Monte Carlo model. Series of simulation results have been obtained. They are helpful for a detailed understanding of diffusion-limited aggregation on heterogeneous surface on the atomic scale. Using this simulation method, we can also simulate thin film growth on a real surface, such as GaAs substrates, reconstructed Au (111) surface, etc.

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