Deposition, diffusion, and aggregation on Leath percolations: A model for nanostructure growth on nonuniform substrates

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Deposition, diffusion, and aggregation (DDA) on percolation substrates were investigated by computer simulations. The nonuniform degree of the substrate is described by the occupied probability p, by which the percolation is generated. p takes values in the range $p_c < p \leqslant 1$, where p_c is the threshold of percolation. The blocked sites in percolation represent the defects in the substrates. The interactions between defects and deposited particles are involved by introducing the sticking coefficient s. For inert defects ($s=0$), the defects hinder the deposited particles from diffusing in the substrates. As p decreases from 1 to p_c, the morphology of the aggregates varies from the DDA pattern on uniform substrates to the few-and-zigzag-branch pattern. For active defects ($s \neq 0$), the defects play a role in absorbing the deposited particles also. With the reduction of p from 1 to p_c, the pattern of aggregates changes from DDA on uniform substrates to a site-percolation-like pattern (for $s=1$) or a dispersed-small-island one (for $0<s<1$) on critical percolation substrates. A rapid increase of the fractal dimension D_f of aggregates appears in the $D_f - p$ curve, which corresponds to the transition of morphologies from a pattern dominated by defects to one controlled by diffusion. Moreover, our simulations show that the Honda-Toyoki-Matsushita relation is reasonable for growth controlled by defect-hindering diffusion in fractional spaces.

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I. INTRODUCTION

Knowledge of atomic behavior on surfaces is important for the production of good quantity thin films. The study of nucleation and growth at early stages of deposition can provide crucial information in this regard.[1,2] Diffusion and reaction are the major microscopic processes that govern the nucleation and growth of monolayers.[3–9] For a long time, there exist three models of nonequilibrium growth: percolation,[10,11] diffusion-limited aggregation (DLA),[11–13] and cluster-cluster aggregation (CCA).[11,14,15] The percolation model implies that the deposited particles do not diffuse any more after deposition. In fact, not only diffusion but also aggregation take place after deposition. In the DLA model, the particles are deposited one by one, so it is only suitable for the case of very low flux for monolayer growth.[1,4] In the CCA model, the particles are put onto the substrate all at once; therefore the CCA model cannot describe the process of continual injection of particles in the deposition process.[11,14]

Jensen *et al.* proposed a model of deposition, diffusion, and aggregation (DDA) to describe submonolayer deposition, i.e., nanostructure growth, on a two-dimensional (2D) uniform surface.[16] In the model, particles are deposited at a certain flux. They continue to diffuse after deposition on the surface, and become immobile once they stick to other particles.[16,17] The morphology of the monolayer depends on the particle flux, the diffusion constant, and the time of the process.[1] To our knowledge, most previous simulations on epitaxial growth were performed on uniform and flat substrates, but many actual substrates are not uniform due to local oxidation, pollution, and other factors. Therefore the investigation of DDA on nonuniform substrates is important. Nonuniform substrates can be described by percolation clusters, where the occupied probability p stands for the degree of nonuniformity of the substrate and the blocked sites in percolation represent defects.[10,18,19] Leath has presented a method to produce single percolation clusters which are generated in the same way as epidemic spreading.[10,20,21] When the probability $p > p_c$, the cluster will grow infinitely.[10,20] The cluster of Leath percolation can be regarded as nonuniform substrate.[10]

In this paper, we simulated deposition, diffusion, and aggregation in Leath percolation and investigated the influence of defects in the substrates on the structure of the nanocluster. These results will be helpful in understanding the formation of clusters on nonuniform substrates in thin-film-growth processes, such as vapor deposition, molecular-beam epitaxy, and so on.

II. MODEL AND METHOD

The present model is similar to the original DDA one[16] except for considering the interaction between deposited particles and defects of the substrate. The Monte Carlo (MC) method was used in the simulations. The procedure of the simulation consists of two parts: producing Leath percolation substrates and generating DDA clusters on the Leath percolation substrates.

The percolation substrate is produced on a 2D square lattice by the Leath method.[10,19,20] In the first step, all the lattice units are empty, except that the origin is occupied. Then, the nearest neighbor sites of the origin are either occupied with probability p or blocked with probability $1-p$. *The blocked sites represent defects*. Again, the empty nearest neighbors of occupied sites are occupied with probability p or blocked with probability $1-p$. In each step, a new shell is added to the cluster. Repeating the process, the expected single percolation cluster can be obtained (for $p > p_c$) or it cannot continue to grow (for $p<p_c$).[10,20] p_c is the critical occupied probability. For the 2D square lattice, $p_c \sim 0.593$.[10] In the present simulations, the occupied probability p takes values in the range $p_c<p\leqslant 1$.

After the percolation substrates are obtained, we start generating DDA clusters on the percolation substrates. The simulation method used is similar to that of Refs. 16 and 17, but it is performed on percolation substrates. In the present method, particles are deposited gradually onto the substrate with a constant flux F. The deposited particles diffuse on the percolation cluster before they meet other particles or blocked sites (defects) in the percolation substrates. They can walk on occupied sites only, and cannot reach the blocked ones (defects). Once they meet other particles, they become immobile and aggregate. What will happen when a deposited particle is close to a defect? A defect can make the local lattice deforming and charge transferring in its vicinity, so the defect can become a trap for the external particles. Thus, we consider that *there exist short-range attractive interactions between the deposited particles and defects*. This interaction is represented by a sticking coefficient s,[4,22,23] just like that in the model of reaction-limited aggregation.[24] When a particle hits the defects, it becomes immobile with probability s, or continues to diffuse with probability $1-s$. The sticking coefficient s is related to the temperature and interactions between the defects and deposited particles.

III. RESULTS AND DISCUSSION

Numerical simulations are performed on a finite square lattice of 400×400 by the MC method. The length of the square particles is chosen to be the unit of length. We focus attention on the influence of the defects on cluster formation on the substrate, so a small flux of particles is taken. In the simulations, we take the flux $F/D=0.5\times 10^{-5}$, where D is the diffusion constant and D^{-1} is proportional to the typical time between two hops. This flux corresponds to injecting a particle onto the substrate every 2×10^{5} MC time steps.

A. Morphology

The difference between deposition, diffusion, and aggregation on a nonuniform substrate and on a uniform one comes from the defects in the nonuniform substrate. There are two effects of defects on aggregates. One is that the defects make the substrate incomplete and they hinder the deposited particles from diffusing in the substrate. Another effect is that the defects absorb the deposited particles.

First, we investigated the characteristics of aggregates due to the effect of defects on the diffusion of deposited particles. In this case, the defects are inert ($s=0$), i.e., there is no attractive interaction between the defects and the deposited particles. Figure 1 shows the morphologies of clusters consisting of the deposited particles with various occupied probabilities p. When $p\sim p_c$, the aggregates appear nonuniform and asymmetrical. There are only a few branches in an aggregate and these branches look zigzag, as shown in Fig. 1(a). As the probability p increases, the aggregates change to uniform ones gradually, and the number of branches in-

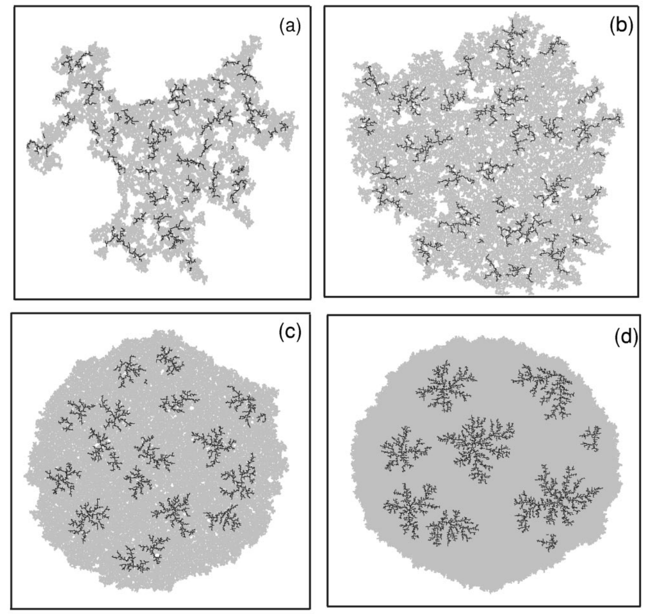

FIG. 1. Morphologies of the clusters formed by deposition, diffusion, and aggregation in Leath percolation with various occupied probabilities p at sticking coefficient $s=0$. $p=0.593$ (a), 0.62 (b), 0.70 (c), and 1 (d).

creases too. When p exceeds a certain value (about 0.75), the morphology of aggregates becomes close to that of DDA clusters on uniform substrates; and if $p\sim 1$, the pattern looks just like it [see Fig. 1(d)]. The evolution of the morphology of aggregates due to variation of p is not difficult to understand. In the case that $p\sim p_c$, the number of blocked sites (defects) in the substrate is very large and close to the critical value. The defects prevent deposited particles from diffusing and forming branches. This results in asymmetric and nonuniform aggregates, as well as a decrease in the number of branches. In addition, the branches have to grow around those defects, so they appear to be zigzag. With p increasing, the number of defects decreases, so the deposited particles can diffuse with less limitation. As a result, the number of branches increases and the patterns gradually become uniform. In the case that $p=1$, the Leath percolation substrate reduces to the compact Eden ''pie'' with dimension of 2 (the space dimension).[1,2] There are very few defects in the Eden ''pie,'' so the aggregates can grow freely just like those on a completely uniform substrate. Therefore, the patterns are very similar to the DDA pattern on uniform substrates.

Now we study the effect of the absorption between defects and deposited particles on morphologies of aggregates. In this case, the defects are active ($s\neq 0$) and the interaction between defects and deposited particles should be taken into consideration. Figure 2 shows the morphologies at $s=10^{-4}$ with various p. It is found that when p is large (say, $p>0.9$ for $s=10^{-4}$) the sticking coefficient s has little effect on the morphology. In this case the morphology is always like the DDA pattern on uniform substrates. But for small p (say, $p<0.7$ for $s=10^{-4}$), s has a great influence on the pattern of aggregates. Even a very small value of s can result in a great change of morphology. When p is close to p_c, the deposited

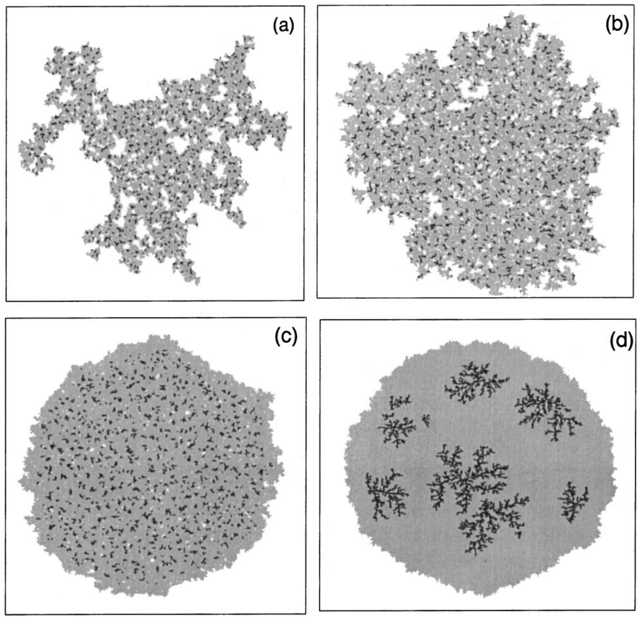

FIG. 2. Morphologies of the clusters formed by deposition, diffusion, and aggregation in Leath percolation with various occupied probabilities p at sticking coefficient $s=10^{-4}$. $p=0.593$ (a), 0.62 (b), 0.70 (c), and 1 (d).

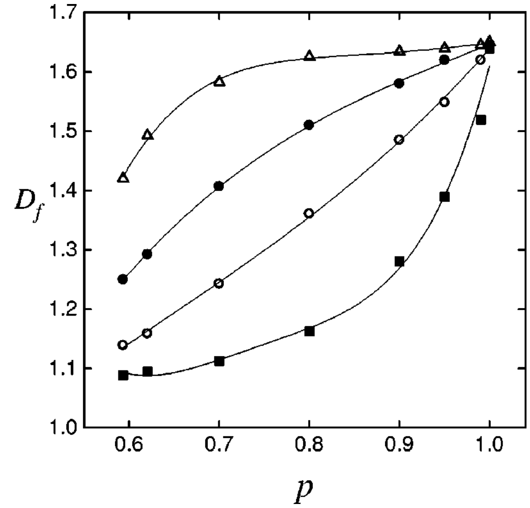

FIG. 3. Fractal dimension D_f of the aggregates in Leath percolation as a function of occupied probability p with various sticking coefficients s. $s=0$ (open triangles), 10^{-4} (full circles), 10^{-3} (open circles), and 1 (full squares). The solid lines are guides to the eye.

particles form a pattern consisting of many very small islands somewhat like site percolation in percolation space, as shown in Fig. 2(a). This pattern for $s=10^{-4}$ is very different from that for $s=0$ [see Fig. 1(a)]. With increasing p, the small aggregates become a little larger. The above results are reasonable. For large p, the number of defects is very few, so the variation of s has little effect on the formation of a monolayer on the substrate. When $p\sim p_c$, there exist many defects in the substrate. These defects not only prevent the particle from diffusing, but also absorb the deposited particles to form small islands. Therefore, the defects partly play the role of a nucleus for aggregates. Thus the patterns appear to be sparse and somewhat like site percolation, even if s is small (in the present case, $s=10^{-4}$).

From the above, we can draw the following conclusions. For $s=0$ (inert defects), the growth process of aggregates is controlled by diffusion. The defects influence the morphology of aggregates by hindering diffusion of deposited particles. As long as the defects are not many ($p>0.75$), the change of pattern due to variation of p is small. But for $s\neq 0$ (active defects), the absorption between defects and deposited particles greatly enhances the influence of defects on the morphologies of aggregates. Therefore, the deposited particles tend to be absorbed by defects and form many small islands. When $p\sim p_c$, as s increases from 0 to 1, the morphology of aggregates changes from the few-and-zigzag-branch structure to the dispersed-small-island pattern, and then to the site-percolation-like one.

B. Fractal dimension of aggregates

The geometric properties of morphologies of aggregates can be described by the fractal dimension D_f. We calculated the fractal dimensions of branched structures and islands by the box-counting method.[25] For a low occupied fraction, apparent fractal behavior was observed between physically relevant cutoffs. The lower cutoff r_0 is presented by the length of particles. The upper cutoff r_1 is given by the average gap between adjacent particles.[25]

Figure 3 plots the simulation results for the fractal dimension of aggregates as a function of the occupied probability p for several sticking coefficients s. It shows that, when $p=1$, the fractal dimension $D_f\sim 1.65$, which is the value for the DDA model on a uniform substrate. The reason is that the substrate with $p=1$ is identified with a 2D plate. Because there are no defects, this value of D_f is independent of s. Once a defect exists (i.e., $p<1$), the fractal dimension decreases with increasing sticking coefficient for a system with identical occupied probability. This behavior can be explained intuitively as follows. The larger the sticking coefficient is, the stronger is the absorptivity between the defect and deposited particle. Therefore, the deposited particles cannot diffuse to a distance and they form the small-island-pattern for nonzero sticking coefficient [see Figs. 2(a)–2(c)], instead of the zigzag-branch-pattern for $s=0$ [see Figs. 1(a)–1(c)]. With enhancement of the absorptivity of the defect, the growth of the branch pattern is hindered more seriously. As a result, the fractal dimension of the pattern is reduced with increasing s. When $p\sim p_c$, there exist a large number of defects in the substrate. In this case, D_f decreases from 1.43 to 1.08 with s increasing from 0 to 1. The former is the value of the DDA pattern in the case of inert defects and the latter is that of the site-percolation-like pattern growing on the critical percolation substrate. Figure 3 also shows that the rapid rise of D_f occurs at $p\sim 0.65$ (for $s=0$) and 0.95 (for $s=1$). This fact indicates that the stronger the absorptivity between the defect and deposited particle, the larger is the influence of defects on morphologies of aggregates, for systems with the same occupied probability. The occupied probability p at which D_f rises rapidly corresponds

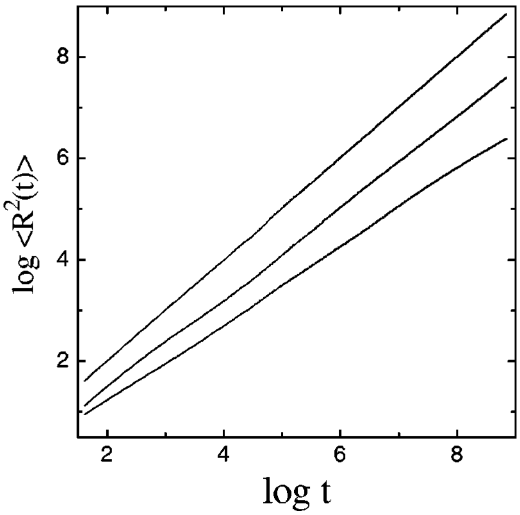

FIG. 4. The log-log plots of the mean square end-to-end distances $\langle R^2(t)\rangle$ of diffusing particles to time step t for defect-hindering diffusion in Leath percolation with various occupied probabilities p. From top to bottom, p was taken as 1, 0.70, and 0.593, respectively.

to the transition of morphology from the pattern dominated by defects to that dominated by diffusion.

C. Honda-Toyoki-Matsushita relation for fractal dimension

In this work, the growth process for large s is dominated by the adsorption of defects. But for $s=0$, the growth is controlled by *defect-hindering diffusion*. For the case of growth controlled by pure diffusion, based on mean field theory, Honda *et al.* presented a relationship connecting the fractal dimension D_f of aggregates with d_s and d_w (Refs. 19 and 26)

$$D_f=(d_s^2+d_w-1)/(d_s+d_w-1). \tag{1}$$

In Eq. (1), d_s is the fractal dimension of the space in which the particles aggregate, and d_w is the fractal dimension of particle motion in the space. Expression (1) is named the Honda-Toyoki-Matsushita (HTM) relation. This relation has been confirmed numerically to be correct only for some special cases, e.g., growth controlled by pure diffusion, and ballistic motion in uniform spaces.[26] *Is the HTM relation still applicable for aggregation controlled by defect-hindering diffusion* $(s=0)$ *on substrates with fractional dimensions*?

To answer the above question, we studied the behavior of defect-hindering diffusion on Leath percolation substrates. The fractal dimension d_w of the particle diffusion can be obtained from the scaling relation[10,11]

$$\langle R^2(t)\rangle \sim t^{2/d_w}, \tag{2}$$

where $\langle R^2(t)\rangle$ is the mean square end-to-end distance of the diffusing particle and t stands for the MC time step. We simulated the random walks of Leath percolation through the range $p_c<p\leqslant 1$. Log-log plots of $\langle R^2(t)\rangle$ vs t are shown in Fig. 4. It can be seen that, there is a stable scaling relation of $\langle R^2(t)\rangle$ to t. When $p\sim p_c$, we get $d_w=2.73$ and $d_s=1.89$, which are in accordance with the previous theoretical results that $d_w\sim 3d_s/2$ and $d_s\sim 91/48$.[10] At $p=1$, the Leath percolation reduces to the Eden "pie," with the result that the random walk is very similar to Brownian motion. In this case, $d_w\sim 2$, which is very close to the expected value for Brownian motion $(d_w=2)$.[1] On the other hand, the fractal dimension d_s of Leath percolation substrates can be obtained by the box-counting method.[21,25] After both d_s and d_w are obtained, the fractal dimensions D_f^H of the aggregates grown on Leath percolation substrates can be calculated based on Eq. (1). Table I lists the results for d_w, d_s, and D_f by MC simulations, and that for D_f^H by Eq. (1). It can be seen from this table that the fractal dimensions D_f from the MC simulations are very close to D_f^H from the HTM relation. Therefore, we can draw the conclusion that the HTM relation is still reasonable for the description of growth controlled by defect-hindering diffusion on substrates with fractal dimensions.

TABLE I. Comparison between the fractal dimension D_f of aggregates obtained by the simulations and D_f^H by the Honda-Toyoki-Matsushita relation for a set of occupied probabilities p in the range from p_c to 1. d_s is the fractal dimension of a nonuniform substrate and d_w is that of the trajectory of particle diffusion. The sticking coefficient $s=0$.

p	0.593	0.62	0.65	0.70	0.80	0.90	1.00
d_s	1.89	1.94	1.96	1.98	1.99	1.99	2.00
d_w	2.73	2.43	2.27	2.18	2.08	2.04	2.01
D_f	1.43	1.52	1.56	1.60	1.62	1.63	1.65
D_f^H	1.45	1.54	1.59	1.62	1.64	1.66	1.67

For the case $s\neq 0$, the growth is greatly influenced by the adsorption of defects. During growth, adsorption terminates the normal diffusion process of particles, and results in a random sparse distribution of particles, i.e., the dispersed-small-islands structure. Correspondingly, D_f decreases rapidly. The HTM relation cannot describe the fractal dimension of the aggregates formed by the growth process of adsorption.

IV. CONCLUSION

The difference between deposition, diffusion, and aggregation in uniform substrates and that in nonuniform ones is attributed to the effects of defects on DDA. Those effects include the defects hindering deposited particle from diffusion and absorbing them. As the nonuniformity of substrates and the strength of interaction between the defects and deposited particles vary, we get various patterns including site-percolation-like, few-and-zigzag-branch, dispersed-small-island, and the original DDA clusters. These results may be useful in describing vapor deposition, molecular-beam epitaxy, and similar experiments on nonuniform substrates.

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[1] A.-L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, England, 1995).
[2] P. Meakin, *Fractals, Scaling and Growth Far From Equilibrium* (Cambridge University Press, Cambridge, England, 1998).
[3] J.W. Evans, Rev. Mod. Phys. **65**, 1281 (1993).
[4] P. Jensen, Rev. Mod. Phys. **71**, 1695 (1999).
[5] Z. Zhang and M.G. Lagally, Science **276**, 377 (1997).
[6] W.W. Pai, J.F. Wendelken, C.R. Stoldt, P.A. Thiel, J.W. Evans, and D.-J. Liu, Phys. Rev. Lett. **86**, 3088 (2001); V.M. Burlakov, G.A.D. Briggs, A.P. Sutton, and Y. Tsukahara, *ibid.* **86**, 3052 (2001); S.B. Zhang and S.-H. Wei, *ibid.* **86**, 3052 (2001).
[7] H. Brune, C. Romalnczyk, H. Röder, and K. Kern, Nature (London) **369**, 469 (1994); H. Röder, E. Hahn, H. Brune, J.-P. Bucher, and K. Kern, *ibid.* **366**, 141 (1993).
[8] T.-C. Chang, I.-S. Hwang, and T.T. Tsong, Phys. Rev. Lett. **83**, 1191 (1999); B.G. Liu, J. Wu, E.G. Wang, and Z. Zhang, *ibid.* **83**, 1195 (1999).
[9] Y.-P. Zhao, J.B. Fortin, G. Bonvallet, G.-C. Wang, and T.-M. Lu, Phys. Rev. Lett. **85**, 3229 (2000).
[10] *Fractals and Disordered Systems*, edited by A. Bunde and S. Havlin (Springer, Berlin, 1991).
[11] T. Vicsek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1992).
[12] T.A. Witten and L.M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
[13] Z.J. Tan, X.W. Zou, W.B. Zhang, and Z.Z. Jin, Phys. Rev. E **60**, 6202 (1999); Phys. Lett. A **268**, 112 (2000).
[14] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983); M. Kolb, R. Botet, and R. Jullien, *ibid.* **51**, 1123 (1983).
[15] Z.J. Tan, X.W. Zou, W.B. Zhang, and Z.-Z. Jin, Phys. Rev. E **62**, 734 (2000).
[16] P. Jensen, A. Barabási, H. Larralde, S. Havlin, and H.E. Stanley, Phys. Rev. E **62**, 734 (1994); Nature (London) **368**, 22 (1994); Phys. Rev. B **50**, 15316 (1994).
[17] Z. J. Tan, Ph.D. thesis, Wuhan University, (Wuhan, China, 2001); Z.J. Tan, X.W. Zou, and Z.Z. Jin, Phys. Lett. A **282**, 121 (2001).
[18] M. Murat and A. Aharony, Phys. Rev. Lett. **57**, 1875 (1986).
[19] Z.J. Tan, X.W. Zou, S.Y. Huang, and Z.Z. Jin, J. Phys. Soc. Jpn. **70**, 3251 (2001).
[20] P.L. Leath, Phys. Rev. B **14**, 5046 (1976).
[21] Z.J. Tan, X.W. Zou, and Z.Z. Jin, Phys. Rev. E **62**, 8409 (2000).
[22] H. Larralde, P. Jensen, M. Meunier, and A. Pimpinelli, in *Structure and Evolution of Surfaces*, edited by R. C. Cammarata, E. H. Chason, T. L. Einstein, and E. D. Williams, MRS Symposia Proceedings No. 440 (Materials Research Society, Pittsburgh, 1997).
[23] In the model of Ref. 22 for cluster formation on surfaces, if a particle hits a defect, it will be trapped for ever. In the present model, the particle becomes immobile with probability s and continues to diffuse with probability $1-s$.
[24] P. Meakin, Phys. Rev. A **27**, 1495 (1983), see also Refs. 2,8,11.
[25] D.A. Hamburger, O. Biham, and D. Avnir, Phys. Rev. E **53**, 3342 (1996).
[26] K. Honda, H. Toyoki, and M. Matsushita, J. Phys. Soc. Jpn. **55**, 707 (1986); see also Refs. 2,11.