Vol 14 No 9, September 2005
1009-1963/2005/14(09)/1873-06

Chinese Physics

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Post-deposition dynamics of multiple cluster aggregation on liquid surfaces*

Wu Feng-Min(吴锋民)[a)b)†], Xu You-Sheng(许友生)[a)],
Ye Gao-Xiang(叶高翔)[b)], and Wu Zi-Qin(吴自勤)[c)]

[a)] *College of Mathematics and Physics, Zhejiang Normal University, Jinhua 321004, China*
[b)] *College of Science, Zhejiang University, Hangzhou 310027, China*
[c)] *Department of Astronomy and Applied Physics, University of Science and Technology of China, Hefei 230026, China*

(Received 15 November 2004; revised manuscript received 27 April 2005)

A comprehensive simulation model—deposition, diffusion, rotation and aggregation—is presented to demonstrate the post-deposition phenomena of multiple cluster growth on liquid surfaces, such as post-deposition nucleation, post-deposition growth and post-deposition coalescence. Emphasis is placed on the relaxations of monomer density, dimer density and cluster density as well as combined cluster-plus-monomer density with time after deposition ending. It is shown that post-deposition coalescence largely takes place after deposition due to the large mobility of clusters on liquid surfaces, while the post-deposition nucleation is only possible before the saturation cluster density is reached at the end of the deposition. The deposition flux and the moment of deposition ending play important roles in the post-deposition dynamics.

Keywords: post-deposition dynamics, aggregation, liquid surface, simulation
PACC: 6460Q, 6810

1. Introduction

Post-deposition phenomena are interesting in the sense of the basic research and potential technological applications. Brune *et al*[1,2] introduced the terms of post-deposition nucleation (post-nucleation) and post-deposition growth (post-growth) of thin film growth on solid substrate. In the former case, some monomers (isolated particles) are still present after the end of deposition and will undergo further nucleation events, resulting in the increase in the number of stable islands after deposition, while the rest of the monomers will aggregate with existing islands. In the latter case, all these monomers attach to existing islands, so the monomer density will decay with time, while the island density remains constant.[3] Post-deposition dynamics has been revealed in systems of Cu/Ni(100),[1] Ag/Pt(111),[2] and Ag/Ag(100)[3] and also in molecular organic thin films.[4] However, to our knowledge, no studies regarding post-deposition phenomena of cluster growth on liquid surfaces can be found in the literature. The great interest in the study of diffusion and aggregation of particles on liquid surfaces has been aroused in recent years, since it is crucial to the microstructure of various atomic aggregates and thin films.[5–9] The phenomena of post-deposition on liquid surfaces are also interesting and worth being investigated.

In this paper, the post-deposition dynamics of multiple cluster aggregation on liquid surfaces is investigated by the use of the deposition–diffusion–rotation–aggregation (DDRA) simulation model, where the clusters can migrate (including diffusion and rotation) easily on the surfaces. The term of post-deposition coalescence is introduced, where clusters are incorporated to form larger clusters after deposition. It takes place largely after deposition due to the large mobility of clusters on liquid surfaces. We concentrate on studying the time dependences of monomer density, dimer density and cluster density as well as combined cluster-plus-monomer density

*Project supported by the Natural Science Foundation for Young Scientists of Zhejiang Province, China (Grant No RC02069) and Zhejiang Provincial Natural Science Foundation of China (Grant No 101032).
†E-mail: wfm@zjnu.cn

and revealing the post-deposition phenomena, such as post-deposition nucleation, post-deposition growth and post-deposition coalescence.

2. Simulation model

To simulate the processes of multiple cluster growth on liquid surfaces, the deposition–diffusion–rotation–aggregation model is presented, and described as follows:

(1) Deposition. Particles are deposited at randomly chosen positions on the liquid surface at a flux F (Monolayer/Monte Carlo step, ML/MCs). Deposition can stop at any moment.

(2) Diffusion. The deposited particles and the clusters are allowed to diffuse randomly in direction, but the diffusion mobility of a cluster decreases with the increase of the cluster mass. The maximum diffusion length can be described as[10]

$$D_{\mathrm{m}} = D_0 s^{-\gamma_{\mathrm{D}}}, \tag{1}$$

where s is the number of particles in the cluster, D_0 is the diffusion length for a single particle (D_0=10 is adopted in this paper), and γ_{D} characterizes the dependence of the maximum diffusion length D_{m} on the cluster mass s. For liquid surfaces, $\gamma_{\mathrm{D}} < 1$ and we assume it remains unchanged in the cluster growth process. The diffusion length for the cluster can be randomly chosen from among 0, 1, 2, ..., and D_{m}.

(3) Rotation. Apart from diffusion, the clusters are allowed to rotate rigidly around each centre of mass. It is evident that the rotation mobility of a cluster also decreases with the increase of the cluster mass. Similar to the case of cluster diffusion, the maximum rotation angle of a cluster can also be described as[11]

$$\theta_{\mathrm{m}} = \theta_0 s^{-\gamma_\theta}, \tag{2}$$

where s is the number of particles in the cluster, θ_0 is set to 2π (rads), and γ_θ characterizes the dependence of the maximum rotation angle θ_{m} on the cluster mass s. The rotation angle for the cluster can be randomly chosen from $-\theta_{\mathrm{m}}$ to θ_{m}.

(4) Aggregation. There are three main processes during aggregation, i.e. nucleation, growth and coalescence. When two mobile particles diffuse to their nearest-neighbour positions, they will stick to each other irreversibly with a unit probability and become a dimer (nucleation). When a mobile particle attaches to the nearest-neighbour position of an existing cluster, it will join the existing cluster and becomes part of the cluster (growth). When two or more clusters arrive at their nearest-neighbour positions, they will stick to each other irreversibly and become a larger cluster.

In our simulation, periodic boundary conditions and non-overlap condition are set up. If a diffusion step length or a rotation angle is so large that the overlap between two clusters happens, then they will aggregate and become one cluster at the position of the two clusters that are just in contact with each other. For simplicity, effects of re-evaporation from the surface and sedimentation of deposited particles are neglected.

3. Results and discussion

We first present the sequence of growth morphologies for diffusion–rotation–aggregation (DRA), where 0.2ML particles are first deposited randomly on a two-dimensional liquid surface. The simulation is performed in a 360×360 area and the factors of diffusion and rotation are set to γ_{D}=0.5 and γ_θ=1.5 respectively, which is in accordance with the main experimental characteristics of metal islands migration on silicon oil surfaces and melting glass surfaces. It is typical of such systems that the particles and clusters can diffuse further and may form larger fractal clusters by joining other aggregates. Figure 1 shows four stages of such a process. As expected, larger randomly branching aggregates appear in the system, and the cluster size increases in time, while the number of cluster decreases. In principle, after a sufficiently long period all of the particles in the finite system become part of a single cluster, while a percolation effect happens.

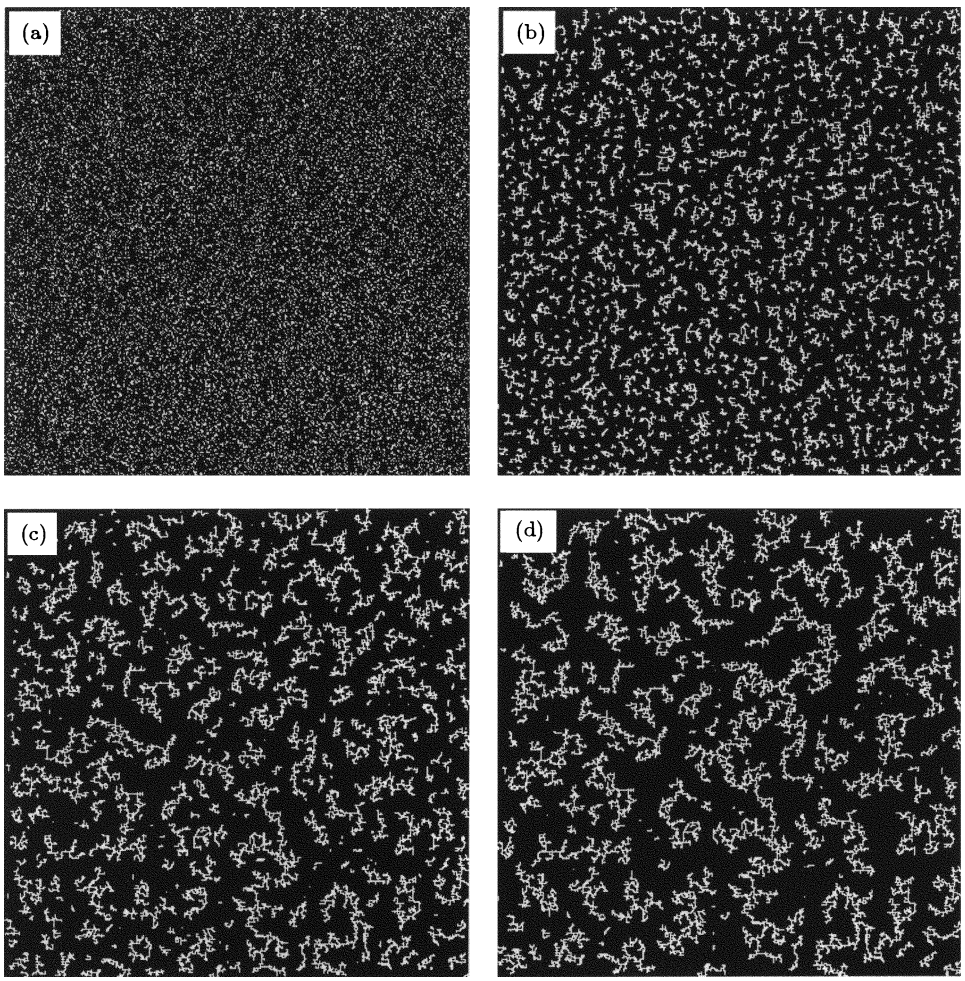


Fig.1. Evolution of growth morphologies for DRA on 360×360 surface, where γ_D =0.5, γ_θ=1.5, and θ=0.2ML. (a) t=1, (b) t=20, (c) t=50, (d) t=100 MCs.

In order to demonstrate the post-deposition phenomena of multiple cluster growth on liquid surfaces, the DDRA simulation images during and after deposition are recorded in sequence. Figure 2 shows the images of the system at four different moments for a flux F=0.002 ML/MCs, γ_D =0.5, γ_θ=1.5. At a very short time, main monomers are found on the surface, since they do not meet another one to form a cluster. Then, small clusters are grown on the substrate. These small clusters can be considered as the nucleation centres for the growth as more and more particles are deposited on the surface. Nucleation and growth are in a competing process, because an arriving particle can either form a new cluster with another free particle or diffuse into an existing cluster. As time goes on (correspondingly the coverage is increasing), large clusters grow at these nucleation centres due to the coalescence between clusters and also the addition of single particles. When the growth time reaches 100 MCs (the corresponding coverage θ=0.2 ML) the deposition stops, while most of monomers still exist on the surface, as seen in Fig.2(b). Later, these monomers and the active clusters can diffuse further and may form larger clusters by joining other aggregates, while the monomers and small clusters decay with time and vanish after a sufficiently long time, as shown in Figs.2(c) and 2(d).

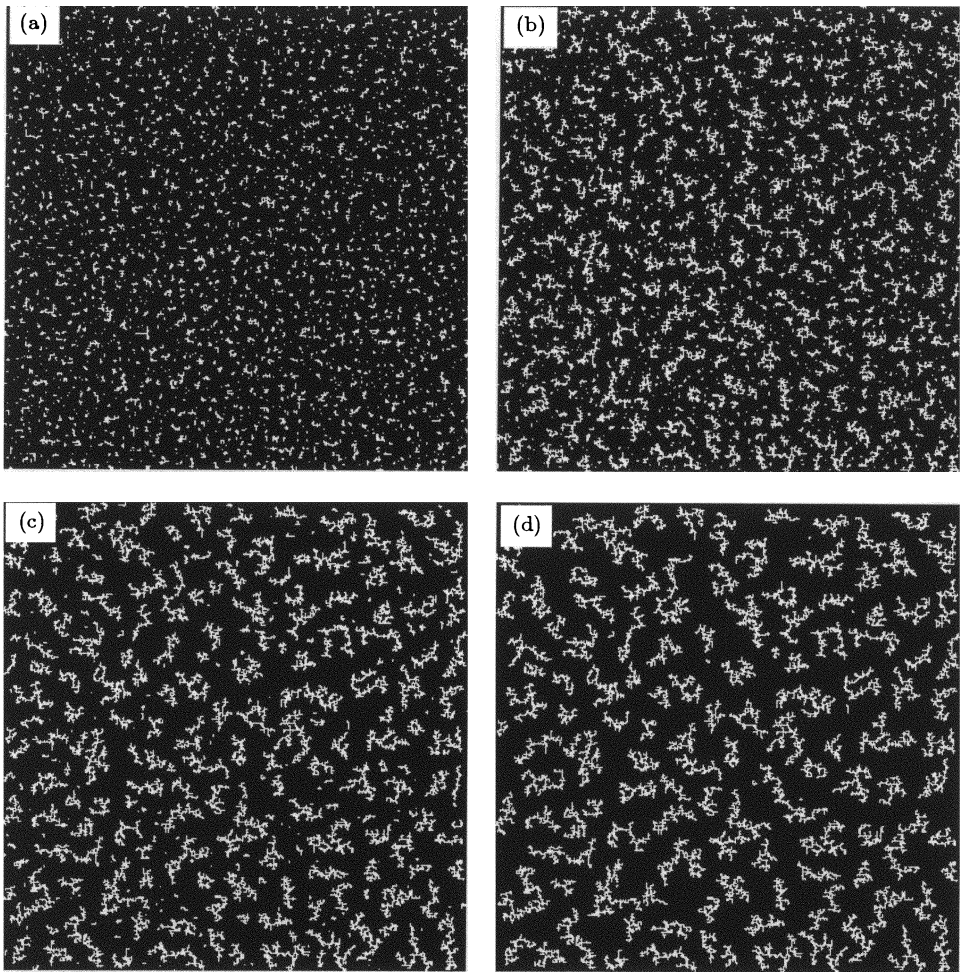


Fig.2. DDRA simulation images recorded in sequence during and after deposition, where γ_D =0.5, γ_θ=1.5, and F=0.002 ML/MCs. (a) t=50 MCs (the corresponding coverage θ=0.1 ML), (b) t=100 MCs, which is the moment when the deposition stops (the corresponding coverage θ=0.2 ML), (c) t=150 and (d) t=250 MCs, respectively.

A quantitative evaluation of the combined cluster-plus-monomer density for DRA and DDRA simulation is presented in Fig.3. The logarithm of the combined cluster density n for DRA decreases monotonously with growth time. However, for DDRA, n increases quickly in time and then reaches a saturation value, where the increment in the total number of cluster and monomer due to the addition of deposition and the decrement in this number due to the aggregation reach an equilibrium state. In this saturation, the combined density n is reduced because of the coalescence effect, while it remains constant during the growth of thin films on solid surface at a low growth temperature.[3] After the deposition is terminated, there are no more new particles deposited on the surface, it seems that the coalescence effect plays a dominant role, giving rise to the dramatic decrease in the combined density of cluster-plus-monomer. Detailed description of the post-deposition dynamics will be discussed later.

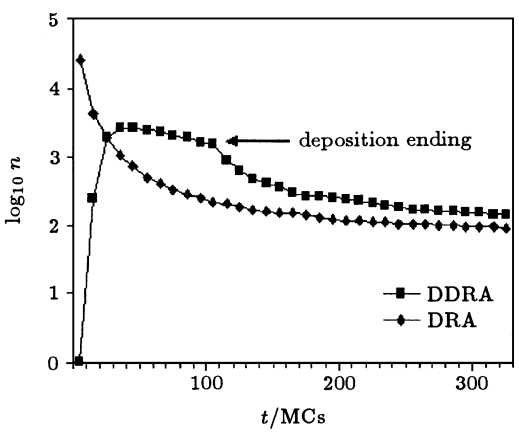


Fig.3. Combined densities of cluster-plus-monomer as a function of the growth time for DRA and DDRA which are shown partly in Figs. 1 and 2, respectively.

To obtain a quantitative insight into the post-deposition dynamics, the density of monomer n_1, the density of dimer n_2, the density of cluster n_x and the combined density of cluster-plus- monomer n are

recorded during and after deposition. Figure 4 shows the simulated time evolution of densities for DDRA, where γ_D =0.5, γ_θ=1.5, F=0.001 ML/MCs and deposition stops at 30 MCs to a coverage of 0.03 ML. The end of the deposition is marked by a dotted vertical line. In this case, the system does not reach the saturation when the deposition stops. The monomer density n_1 increases during deposition by the deposition flux. The monomer concentration is high at the moment of deposition ending. It is reduced after deposition by two processes: nucleation and growth. As expected, a significant fraction of the monomers is engaged in nucleation events and the remaining fraction is consumed by growth of existing or new clusters. To confirm the occurrence of post-deposition nucleation, a particular emphasis is placed on the investigation of the density of dimer n_2 during and after deposition. As shown in Fig.4, n_2 increases not only during but also after deposition. It is illustrated that the increment in n_2 by nucleation is larger than the decrement in n_2 by coalescence. It is an evidence that post-deposition nucleation takes place under the circumstances. The combined density in the later stages of growth exhibits a clear downward trend, because of the decay of the monomers. On the other hand, the monomer decay and the deposition lead to an increase in the cluster density n_x in the earlier stages of growth and then n_x decays much more slowly due to the weak coalescence effect occurring at a low coverage. In a word, in the case of deposition ending before the system reaches a saturation, the dominant behaviours of post-deposition are characterized by the post-deposition nucleation and post-deposition growth.

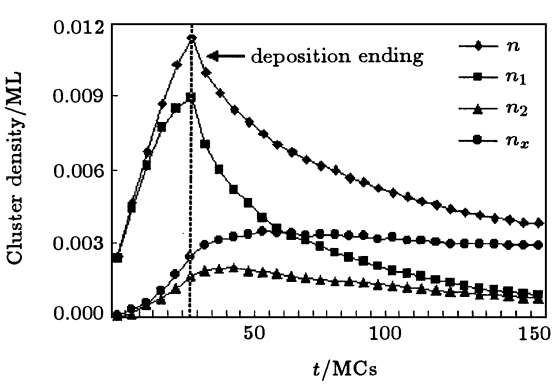


Fig.4. Simulated time evolutions of densities of monomer, dimer, cluster and cluster-plus-monomer for DDRA, where γ_D =0.5, γ_θ=1.5, and F=0.001 ML/MCs and the deposition stops at 30 MCs to a coverage of 0.03 ML.

It is important to note that the post-deposition dynamics depends dramatically on the moment of deposition ending. Figure 5 shows the simulated time evolutions of densities of monomer, dimer, cluster and cluster-plus-monomer for DDRA, where γ_D =0.5, γ_θ=1.5, and F=0.001 ML/MCs and the deposition stops at 100 MCs to a coverage of 0.1ML. In this case, the system is in the saturation state, the monomers attach to existing clusters and are engaged in post-deposition growth, resulting in the decrease in the combined density n. The monomer density n_1 declines rapidly and effectively vanish after 200 MCs. The density of dimer n_2 does not increase any more after deposition, and the post-deposition nucleation does not happen any longer, either. It can be seen clearly from Fig.5 that the density of cluster n_x also declines rapidly because of the strong coalescence effect at a relatively high coverage. It should be noted that the monomer decay after deposition occurs practically and exclusively via post-deposition growth processes under the circumstances and the dominant behaviours are featured by the post-deposition growth and post-deposition coalescence in a range of growth times from 100 to 200 MCs, as seen in Fig.5.

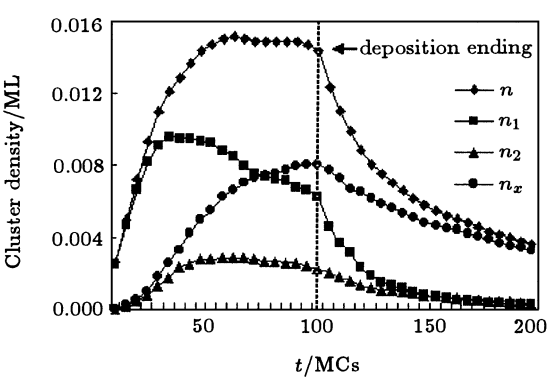


Fig.5. Simulated time evolutions of densities of monomer, dimer, cluster and cluster-plus-monomer for DDRA, where γ_D =0.5, γ_θ=1.5, and F=0.001 ML/MCs and the deposition stops at 100 MCs to a coverage of 0.1ML.

In addition to the moment of deposition ending, it is worth mentioning that the deposition flux also plays an important role in the post-deposition dynamics. Figure 6 shows the simulated time evolutions of densities of monomer, dimer, cluster and cluster-plus-monomer for DDRA, where γ_D =0.5, γ_θ=1.5, F=0.002 ML/MCs and the deposition stops at 30 MCs to a coverage of 0.06 ML. In the case of a higher deposition flux, it is easy for the system to reach a saturation state. The system comes to a saturation state even the moment of deposition ending is as early

as 30 MCs. The post-deposition nucleation does not take place after the deposition ending, where nearly all monomers are incorporated to the existing clusters. The dominant behaviours are featured by post-deposition growth and post-deposition coalescence in the growth times ranging from 30 to 100 MCs. However, after a certain growth time (t is larger than 100 MCs, as seen in Fig.6), the monomers and dimers effectively vanish, and the post-deposition growth is also ended. In this regime, the solely post-deposition dynamical behaviour is characterized by the post-deposition coalescence, resulting in the continuous decrease in n and n_x, while they will approach the same value.

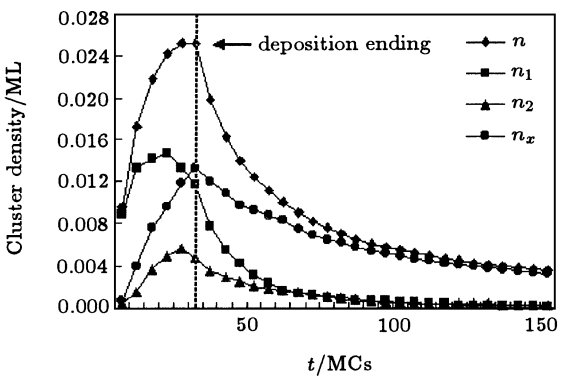


Fig.6. Simulated time evolutions of densities of monomer, dimer, cluster and cluster-plus-monomer for DDRA, where γ_{D} =0.5, γ_{θ}=1.5, and F=0.002 ML/MCs and the deposition stops at 30 MCs to a coverage of 0.06 ML.

4. Conclusions

In summary, the post-deposition behaviours of the multiple cluster growth on liquid surfaces are investigated by means of the Mont Carlo simulations where the comprehensive model – deposition, diffusion, rotation and aggregation model is employed. The complex dynamical behaviours after deposition ending are revealed by taking into account the time dependences of monomer density, dimer density and cluster density as well as combined cluster-plus-monomer density. It is shown that there are three main dynamical processes occurring on the liquid surfaces after deposition ending, i.e. post-deposition nucleation, post-deposition growth and post- deposition coalescence. The post-deposition growth largely takes place after deposition because of the high monomer concentration after deposition. Meanwhile, the post-deposition coalescence also occurs largely due to the large mobility of clusters on liquid surface. However, post-deposition nucleation is only possible before the saturation cluster density is reached at the end of the deposition. After a sufficiently long growth time when the deposition is ended, there is only post-deposition coalescence in the growth process, while the post-deposition nucleation and post-deposition growth are finished. The post-deposition dynamics depends dramatically not only on the deposition flux but also on the moment of deposition ending. Indeed, the post-deposition dynamical behaviour is sensitively related to the monomer concentration and the coverage present immediately after deposition. Future subjects that can be addressed via DDRA simulation are details of cluster size distributions and quantitative relationship between the post-deposition dynamics and the monomer concentration, etc.

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