

Instability Phenomenon in Dip-coating Process for Self-assembly of Fine Particles and Countermeasures with Design

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Abstract:

Self-assembly of fine particles is one of the promising processes for the production of nano-structures. In this process, aqueous suspension is often used. The spreading of suspension on the substrate is complex phenomenon and sometimes causes problems of instability. This paper discusses the instability phenomenon and proposes countermeasures from various standpoints. It was found that special attention should be paid for the pattern design of site-selective assembly. Finally, complex structures made of different size and material of particles were shown utilizing repeated dip-coating to demonstrate the improved stability.

Keywords: Self-assembly, Particle, Instability,

1. Introduction

Dip-coating with suspension that contains fine particles can produce self-assembly of the particles [1]. Basically, this process has been applied to produce uniform assembly structures on a substrate. Applying lithography, narrow line assemblies of micron-orders width has been produced utilizing of hydrophilic/hydrophobic wettability pattern [2] or selective spreading into grooves [3].

On the other hand, it is already known that spreading on an inclined substrate is complex phenomenon because of the fingering (Fig.1) and pinning [4]. Fingering is a phenomenon that means branching of the contact line of the droplet spreading on a wide flat surface. Pinning is a phenomenon in which motion of the contact line is constrained by some structural discontinuity such as asperities.

During the dip-coating process, such instability changes not only the contact-line profile of suspension from line to distorted curve but also the motion of the contact line from continuous to intermittent. And thus, the self-assembly of the particles becomes unstable.

So far, the effect of this kind of instability on the self-assembly process has not been treated though it is often dealt in the papers relating to surface science. This paper introduces such instability in dip-coating process first. Then various countermeasures including control are discussed to improve the stability of the process.

2. Instability phenomenon in self-assembly

2.1 Discontinuous process

Figure 2 shows an example of self-assembly after dropping suspension on a substrate and dried. The conditions are shown in Table 1. As shown in the figure, self-assembly structures can be observed along both in radial and circumferential direction though the position is random just like spider's web. The assembly process is considered as follows: After dripping, the suspension spreading formed fingering in radial direction along with the evaporation of solvent and shrinkage of spreading. The evaporation proceeded from outside to inside on the droplet, which might cause pinning at some point, and thus circumferential pattern was assembled. Pinning is just like pin the motion of contact line of spreading and can be caused by asperities on the substrate or local variation of evaporation rate.

The overall structure has randomness in shape and its location but it is found that monolayer structures were obtained from the observation with high magnification. It is clear that continuous pattern cannot be obtained with dripping method.

2.2 Continuous process

To obtain continuous structures, dip-coating process was carried out. In this process, hydrophilic substrate was dipped into suspension and then drawn-up slowly. Along with the evaporation of water, meniscus force is generated to attract the particles each other to produce packed-structure (Fig.3).

Figure 4 shows the variation in the structures in this process. Fig 4(a) shows a uniform structure often obtained when drawing-up speed is low. This is a result of continuous process. Ideally, the structure should be monolayered of hexagonally packed. However, this result was multilayered. The difference might be caused by improper concentration of the particles.

Fig. 4(c) shows a typical result of fingering under the condition of high drawing-up speed and/or low concentration of particles. The motion applied to the substrate was simple linear motion. Thus, line-and-space stripe patterns parallel to the motion were obtained. It is found from the close-up view that the assembly is hexagonal-packed and monolayered.

Fig. 4(b) shows specific patterns under the condition between the above two. In this case, pinning phenomenon was observed and contact line drop-down intermittently during drawing-up motion at constant speed. It is interesting that mesh-like structure of similar triangles can be observed. The structures were also hexagonal-packed and monolayered.

The cause of difference in structures is considered as the difference of supply rate of particles at the site of self-assembly which is governed by concentration of suspension and drawing-up speed of the substrate.

Figure 5 shows the effect of drawing-up speed on the coverage of particles on the surface based on the experiments. The coverage is defined as the ratio of occupied area of particles to the area to be occupied. It is found that the coverage decrease inversely proportional to the increase in the speed which means the decrease in supply rate of particles. The tendency is different depending on the particle size and the smaller particles show higher coverage. The mesh-like structure was obtained at narrow range of speed which means unstable condition. Based on these results, various type of structure can be obtained by controlling the conditions. However, before discussing the strategy to obtain specific shape of structures, the factors affecting to the process should be made clear.

2.3 Factors affecting the process

Figure 6 shows the relationship or dependencies between the factors that affect the self-assembly process. There is an interim factor “spreading” of the suspension between the primary factors and

final result.

Spreading of suspension is very complex phenomenon because the contact angle changes with various parameters such as surface energy of the substrate and tension of the suspension. Also, the contact line is often deformed by pinning effect which shows the points where the roughness or surface energy changes. Fingering is another interesting phenomenon. When a liquid drop slides down on a smooth and flat surface, the shape of front edge may separate into many parts just like fingers. In the case of dip-coating, the fingers are formed upward on the substrate as shown in Fig.1. In some cases, various types of convection change the shape of spreading. Marangoni convection is typical one that is caused by imbalance between local surface tensions. It changes continuous motion of the contact line.

Various approaches are possible to obtain site-selective assembly in which particles are assembled only on required portion. So far, the authors have tried wettability pattern that consists of hydrophilic and hydrophobic area, or grooved pattern. Thus, it should be necessary to discuss the design guideline.

3. Countermeasures

To stabilize the dip-coating process, various aspects should be taken into account including pattern design and wettability design.

3.1 Pattern design

In dip-coating process, the motion applied to the substrate is linear motion at constant speed. In such case, the pattern should be continuous along the motion. That is, planer or line-and-space design should be adopted. Intermittent pattern such as dots is difficult to assemble.

Figure 7 shows spreading of suspension near the groove for site-selective assembly. Suspension selectively spreads into the hydrophilic groove by capillary force. To improve the selectivity of the assembly, the plateau or convex part is sometimes coated with hydrophobic material. In this case, the interfacial force acting on the contact line becomes opposite direction against the capillary force and thus, the spreading profile across the groove becomes rather complex as shown in the figure.

Theoretical or model-based estimation is so difficult that experiments were conducted to discuss the design guideline.

Figure 8 shows the effect of groove depth on the coverage of assembly. Groove depth affects the drag or attraction of suspension during the dip-coating. The main cause of this force is capillary force, thus, deep groove is preferable. The experimental results coincide well with the tendency. However, the tendency became different depending on the particle material. The reason of this difference is considered as the difference in the interaction between the particles and substrate including electrostatic forces. Further study is necessary to generalize these relationships.

3.2 Wettability design

Contact angle is often used to measure wettability. Hydrophilic property is necessary to initiate dip-coating process and smaller contact angle is preferable. On the other hand, any portion where the assembly is not required should be hydrophobic to prohibit from spreading of suspension.

Silicon wafer covered with oxide layer is hydrophilic. This characteristic can be changed to hydrophobic by depositing octadecyltrichlorosilane (OTS) layer. Self-assembled monolayer deposition is also possible. On the other hand, hydrophobic surface can be changed to hydrophilic by applying plasma process. In this process, surface contaminants are removed and surface becomes rough with the advance in the ion bombardment.

Figure 9 shows the relationship between contact angle on the plateau in Fig.7 and coverage. OTS was deposited on the plateau with contact printing process [5]. By changing the holding time of stamp on the substrate, contact angle was modified at several steps. It is found that the coverage decrease with the increase in the contact angle, and the contact angle should be smaller than 60 degrees to obtain 100% of coverage in this case. In other words, hydrophilic substrate is preferable to stabilize the process.

3.3 Application

Once the dip-coating process has been stabilized, it can be repeated after some additional process [6].

Figure 10 shows the repeated dip-coating process to produce complex structure made of different size and material of particles. Each dip-coating process is almost same with one discussed before. In the first coating process, particles are assembled at the bottom of grooves while the plateau or ridge parts are coated with hydrophobic material to prohibit from spreading of suspension. Before the second coating process, the assembly is dipped into acid in the case of silica particles to promote siloxane bonding between the particle and silicon substrate as shown in Fig.11. If the particle material is polystyrene (PS), they can be fixed by rising temperature to about melting point. After this process, the substrate was processed with plasma to change the hydrophobic parts to hydrophilic. In the second coating process, particles of another size are assembled on originally hydrophobic parts.

Table 2 shows the experimental conditions for the complex assembly. Different size of assembly and/or different size of materials, polystyrene and/or silica, were assembled on a same substrate by repeated or duplicated dip-coating. Figure 12 shows the results. Figure 12(a) shows the combination of different size of polystyrene particles ($\phi 1\mu\text{m}$, $\phi 3\mu\text{m}$). It is found that different sizes of particles are assembled side by side in monolayer. By tuning the dimension of groove, precisely complex structure was assembled with good repeatability. Figure 12(b) shows combination of different size of silica particles. In this case, the boundary is not clear and two sizes of particles are mixed near the boundary. The fixing process for these results is not same but the particles assembled in the first dip-coating, larger particles in both cases, remained on the substrate. It was found that the fixing procedure is effective.

Figure 12(c) shows the combination of different size and material particles. The center part is monolayered assembly of silica particles of $\phi 1\mu\text{m}$. Besides this assembly, almost monolayered assembly of polystyrene of $\phi 400\text{nm}$ can be seen. At the boundary of these assemblies, dark colored band can be seen. This part is not monolayer but double- or multi-layer of smaller particles, because the larger silica particles did not occupy full width of the groove and there were vacant areas along edge of a groove.

The results shown in Fig.12 are just demonstrations, and they have no functions. If the each particle

has independent functionality such as gas sensor [8], this complex assembly can afford, of course, integrated functions.

4. Discussions

If discontinuous mesh-like or line & space structure as shown in Fig. 4(b), 4(c) is to be produced on flat and smooth substrate, precise control such as drawing-up speed is necessary because these types of dip-coating is quasi-stable and very sensitive to change in conditions. In addition, various conditions change the situation just like temperature change the surface tension and thus spreading profile. In this case, randomness in period of intermittent cycle or its position is inevitable since the process is inherently random. If there is an appropriate sensing device, feedback control will be possible. However, the model of the process should be established in advance.

In this paper, only the continuous pattern like line-and-space was treated. If precise and discontinuous pattern is to be produced, the spreading itself should be discontinuous. For this purpose, dip-coating is not necessarily appropriate because the process is inherently continuous. Dispenser or other devices that can put suspension on the required portion independently and intermittently should be applied [9].

5. Conclusions

Dip-coating is useful process for self-assembly of fine particles. However, instability phenomenon sometimes disturbs the process. This paper aimed to clarify how to stabilize the process with design.

The results are summarized as follows:

- Instability phenomena relating to dip-coating for self-assembly were introduced.
- Some countermeasures to stabilize the process were discussed from different viewpoints such as design of groove depth.
- After stabilizing the process, complex assembly was demonstrated in which particles of difference materials and sizes were assembled along lines side by side.

Acknowledgement

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[1]

Table 1. Conditions for stability observation.

Material	Polystyrene
Diameter	404 nm ($\sigma=5.9\text{nm}$) 994 nm ($\sigma=10\text{nm}$)
Concentration	0.1 wt%
Solvent	Pure water
Substrate	Glass
Contact angle	<5 degrees

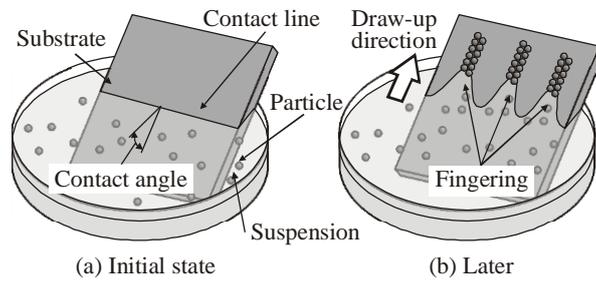


Fig. 1. Fingering instability phenomenon.

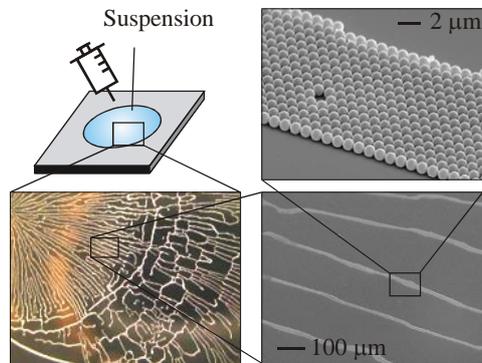


Fig. 2. Self-organizing structure after the evaporation of dripped suspension.

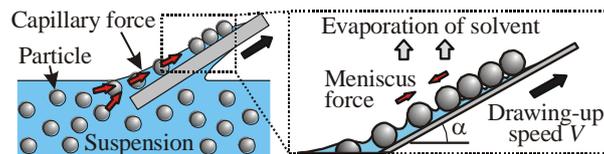


Fig. 3. Dip-coating for self-assembly of particles.

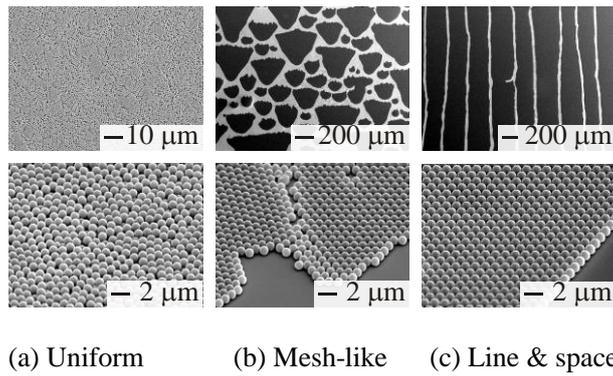


Fig. 4. Variation of self-organizing structure depending conditions.

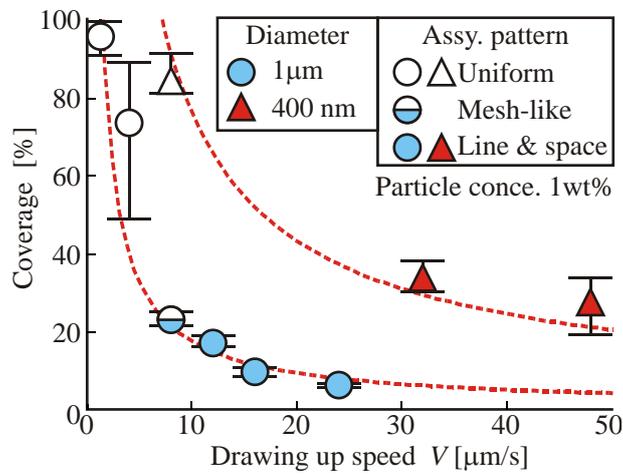


Fig. 5. Factors affecting to the self-assembly and their relationship.

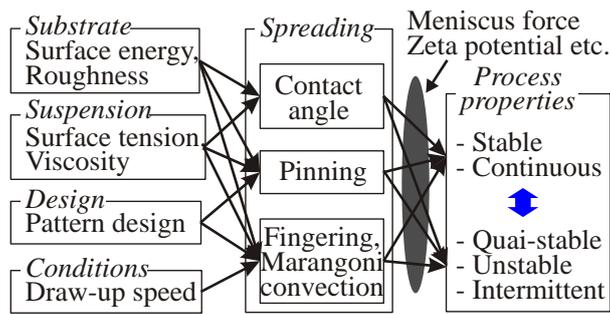


Fig. 6. Factors affecting the process.

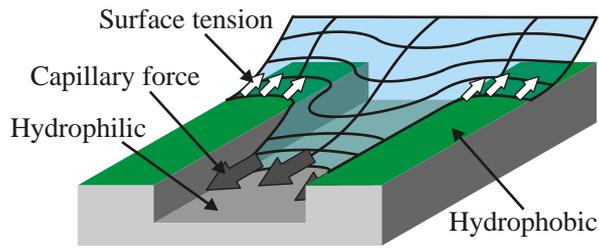


Fig. 7. Grooves for site-selective assembly and complex spreading near the groove.

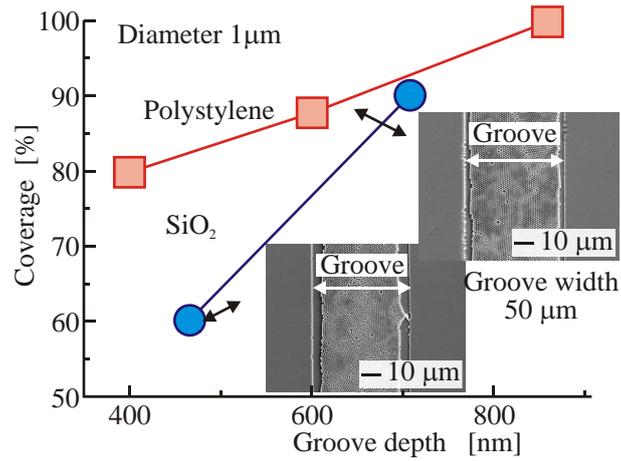


Fig. 8. Effect of groove depth on the coverage of particles in groove.

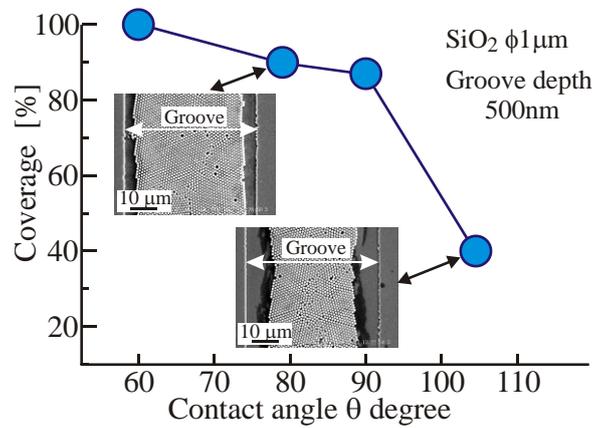


Fig. 9. Effect of contact angle of plateau part of the substrate on the coverage of particles.

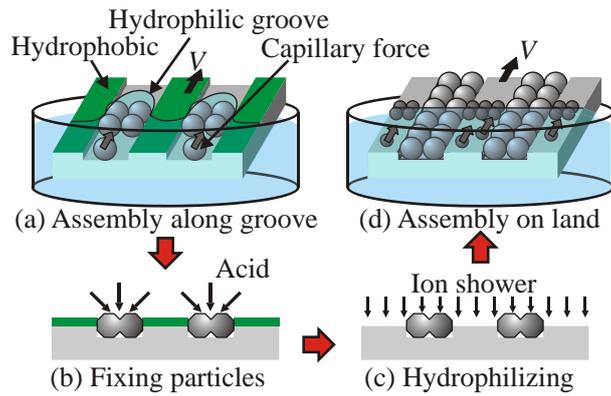


Fig. 10. Repeated dip-coating to produce complex structures (case of silica particles).

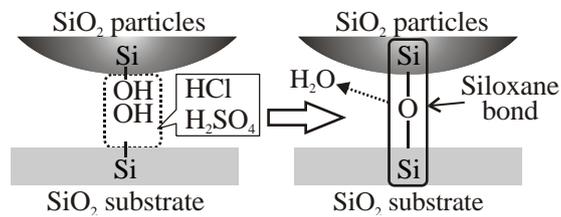
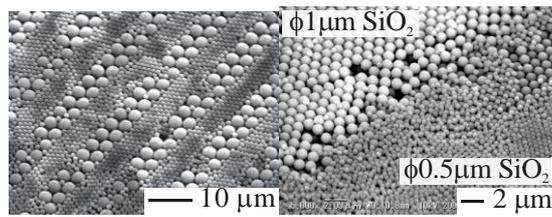


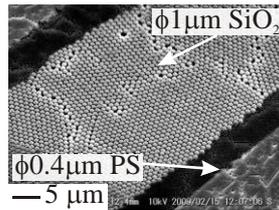
Fig. 11. Fixation of silica particles using siloxane bonding [7].

Table 2. Conditions for complex assemblies.

Fig.12(a)	Particle	PS: $\phi 1 \mu\text{m}$, $3 \mu\text{m}$
	Substrate	Groove width $5 \mu\text{m}$, Pitch $10 \mu\text{m}$, Depth $1.7 \mu\text{m}$
Fig.12(b)	Particle	Silica: $\phi 1 \mu\text{m}$, $\phi 500 \text{nm}$
	Substrate	Groove width $50 \mu\text{m}$, Pitch $100 \mu\text{m}$, Depth 500nm
Fig.12(c)	Particle	Silica: $\phi 1 \mu\text{m}$, PS: $\phi 400 \text{nm}$
	Substrate	Groove width $50 \mu\text{m}$, Pitch $100 \mu\text{m}$, Depth 500nm



(a) Polystyrene particles (b) Silica particles



(c) Combination of polystyrene and silica

Fig. 12. Complex structure made of different sizes and materials of particle.