Fabrication of Colloidal Particle Array by Continuous Coating Process

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The method using a colloidal liquid film coated on the solid substrate, which results the convective self-assembly, is one of the most promising approaches to prepare the particle array having a large area with high regularity for novel functions. The objective of this study is to understand the fabrication phenomena of colloidal particle array by the continuous coating process.
The micrometer-sized particles were deposited by feeding the colloid suspension into the feeder and dragging the substrate. The deposited particles in the thin wetting film are crystallized to the monolayer particle array by convective self-assembly. At the steady-state of the continuous coating process, a simple equation balancing the volumetric fluxes of particles was proposed, which agreed well with the experimental results. The drying region of a thin wetting film increased with the humidity, but the coating speed of particle assembly did not changed. The defects of the particle array were observed. The number of defects decreased at the continuous coating process comparing with the batch operation. The effect of the contact angle of the substrate on the fabrication of particle array was also carried out.

1. Introduction

Three-dimensional arrays of particles are expected as the structure having novel functions such as light-emitting diodes (Coe et al., 2002), solar batteries (Huynh et al., 2003), photo-switch (Ohtsu et al., 2002), and photonic crystals (Fudouzi and Xia, 2003). The colloid-based antireflective coating (Prevo et al., 2007) is one of the two-dimensional particle array applications. The method using a colloidal liquid film coated on the solid substrate, which is used convective self-assembly phenomena, is one of the most promising approaches to prepare the regular packing structure of particles. Dimitrov and Nagayama (1996) reported that this method could be made highly ordered particle array when the substrate was pulled up from colloidal suspension. Prevo and Velev (2004) proposed the horizontal coating method using high concentrated colloidal suspension for the rapid deposition of particles to make a large area. But their proposed method was the batch type operation, so that the fabrication method of the particle array having a large area with high regularity may be still under development. Nonaka et al. (2007) developed the continuous coating process for large area fabrication of the particle array, which was a similar operation of that proposed by Prevo and Velev (2004). The objective of this study is to understand the fabrication phenomena of colloid particle array prepared by a continuous coating process.

2. Experimental

2.1 Continuous coating method

Figure 1 shows the schematic diagram of the apparatus of the continuous coating method. The colloidal suspension was fed to the fixed feeder by a micro syringe pump (KDS100, KD Scientific, Hollistor, MA, USA), and flowed out from the slit with 250 μm height and 12 mm width of the fixed feeder. The substrate was drawn at the constant rate by a stepping motor (Orientalmotor, Tokyo, Japan), to make a particle array. Polystyrene particles (PSL) whose diameter was 1.0 μm (PS2538B, Magsphere, Pasadena, CA, USA), 5.0 μm (PS2829B, Magsphere) or 10 μm (PS/DVB2633B, Magsphere) was used as model particles. The experiment was carried out at the room temperature (about 293 – 298 K) with controlled relative humidity of 30, 50, or 70%.

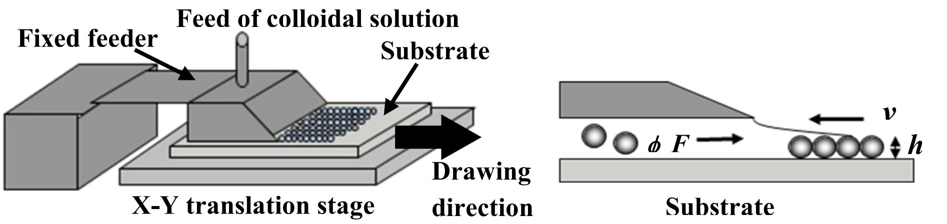

Figure 1: schematic diagram of the continuous coating method and definition of operation parameters.

2.2 Hydrophilic treatment of substrate

The substrate used was a cover glass (No. 5, Matsunami Glass, Kishiwada, Japan) with different cleaning procedures to examine the effect of hydrophobicity or a contact angle of the substrate on particle array structure. Table 1 shows four kinds of cleaning procedures at 353 K and the resulted contact angle of colloidal suspension on the substrate.

Table 1: Cleaning procedure and contact angle of substrate after cleaning

No.	solution	cleaning period [minutes]	contact angle [degree]
1	water	10	30
2	ethanol	10	15
3	RCA cleaning solution	1	10
4	RCA cleaning solution	10	less than 5

Where RCA cleaning solution is a fresh mixture of distilled water, 30% hydrogen peroxide aqueous solution, and 28% ammonia aqueous solution whose volume ratio is 5 : 1 : 1. Most experiments were done using the substrate with ethanol treatment (cleaning No. 2).

2.3 Evaluation of particle array

Evaluation methods for the regularity of particle array were proposed such as Laue pattern measurement and UV-visible absorbance spectra. We proposed the very simple method (Nonaka et al., 2007), which was counted the number of defects along the straight line on the image of particle array as shown in Figure 2. We drew straight lines at the interval of 5 times width of particle size, counted the number of the defects per 100 particle in which the straight line was crossed, and classified into the point defect and the line defect as shown in the right hand of Figure 2. The point defect was defined as the hole of one particle, corresponding with lattice defect, while the line defect indicated the multi domain of colloid crystal array.

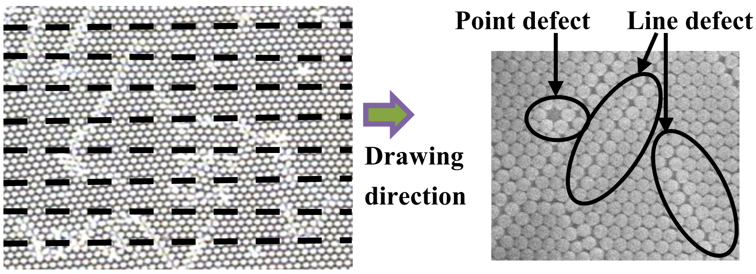

Figure 2: Evaluation and classification of defects in particle array

3. Results and discussion

3.1 Flow rate of feed suspension

At the steady-state of a continuous coating process, a simple equation balancing the volumetric fluxes of particles can be expressed as follows;

$$\phi F = h v W \left(1-\varepsilon\right) . \quad (1)$$

Where ϕ is volume fraction of particles in the feed suspension, which is fed to the feeder with constant flow rate, F. v is the drawing speed of the substrate, i.e. coating speed of particle assembly. h, W and ε are the height, the width, and porosity of the particle assembly layer, respectively. Figure 3 shows the effect of the flow rate of the feed suspension, F, on the coating speed, v, using 5.0 μm PSL of ϕ = 10% at 30% relative humidity. The structure of particle array was changed from multilayer, monolayer, and submonolayer, as v increased at constant F. The broken line in Figure 3 was the calculation line by using Equation (1) with the monolayer condition, that is h is equal to particle diameter, d, and ε = 0.395. The calculation line agreed well with the experimental observation data.

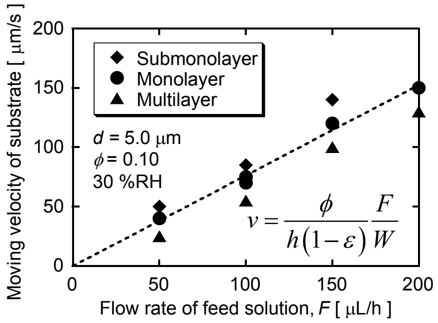

Figure 3: Effect of flow rate of feed suspension on coating speed using 5.0 μm diameter of PSL.

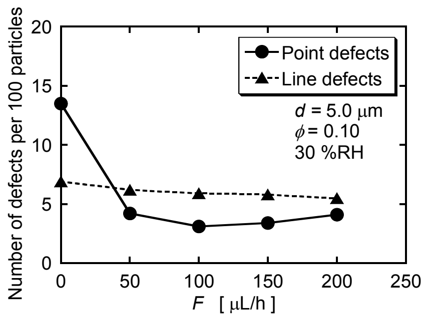

Figure 4: Effect of flow rate of feed suspension on defects of monolayer particle array.

Figure 4 shows the effect of F on the number of defects when monolayer particle array was produced at 30% relative humidity. The number of the point defect drastically decreased to 1/2 – 1/3 from that at F = 0 condition, when a certain value of F was operated at various operation conditions including the humidity of surrounding. The operation of F = 0 was corresponding to the batch coating type experiment by using a similar equipment reported in Prevo and Velev (2004). This means that the continuous coating process is suitable to make less defect assembly than the batch coating system. On the other hand, the number of the line defect of the particle array decreased slightly as F increased.

3.2 Particle size and volume fraction of particles in feed suspension

Figure 5 shows the relationship between the flow rate of the feed suspension, F, and the coating speed, v, at the monolayer condition using 5.0 or 10.0 μm PSL. The experimental results using both particles agreed with the calculation line of monolayer condition (h = d), where d is particle diameter. When small particles were used, v should increase to prepare monolayer particle array.

Figure 6 indicates the effect of volume fraction of particles in feed suspension, ϕ. When ϕ was changed from 2.5 to 10%, the monolayer particle array could be fabricated by adjusting operated parameters such as v and F, as expected from Equation (1).

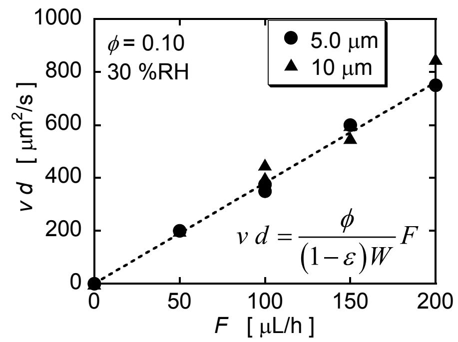

Figure 5: Effect of particle diameter of feed suspension on coating speed using 5.0 or 10 μm diameter of PSL.

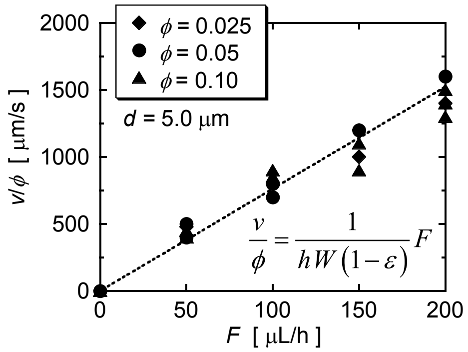

Figure 6: Effect of particle volume fraction of feed suspension on coating speed using 5.0 μm diameter of PSL.

3.3 Relative humidity of surroundings during particle array formation

The effect of the relative humidity of surrounding on the particle assembly behaviour was studied. The solvent evaporation flux was depended on the humidity. The drying region of a thin wetting film increased with the humidity, but the coating speed of particle assembly did not changed as expected from Equation (1). The number of the line defects decreased as the relative humidity increased, especially from 30 to 50%. But the number of the point defects did not depend on the humidity so much.

3.4 Contact angle of substrate

When PSL with 1.0 μm diameter was used, the particle assembly was prepared on the substrate with less than 30 degree of the contact angle of the substrate. However, the particle assembly of 5.0 μm diameter PSL was not observed at the condition of less than 5 degree contact angle, while those PSL could be arranged on the substrate with 10 – 30 degree contact angle. This result indicated that the thickness of the front edge of a thin wetting film was too small for 5.0 μm diameter PSL to deposit on the substrate at the condition of less than 5 degree contact angle.

4. Conclusions

We proposed the continuous coating process to fabricate the particle array thin film by coating at a high speed, and then found the following conclusions.

The coating speed to prepare the particle array can be predicted by using the proposed mass balance equation of particles. The defects were categorized the point defect and the line defect, and the number of point defects decreased when using the continuous coating process. The number of defects also decreased when coating was conducted under high relative humidity. The contact angle of the substrate should decrease when the particle diameter became small.

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