Packing of submicrometer-sized polystyrene particles within the micrometer-sized recessed patterns on silicon substrate

Manabu Tanaka\textsuperscript{a}, Naonobu Shimamoto\textsuperscript{b}, Takashi Tani\textsuperscript{b}, Iwao Ohdomari\textsuperscript{b}, Hiroyuki Nishide\textsuperscript{a,*}

\textsuperscript{a}Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan
\textsuperscript{b}Department of Electrical Engineering and Bioscience, Waseda University 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

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Abstract

The packing of submicrometer-sized polystyrene particles within the micrometer-sized recessed patterns were achieved using silicon-microfabricated substrates and a simple dipping and pulling-up process. The polystyrene particles were selectively deposited within the micrometer-sized square, triangular, or circular recessed patterns by tuning the experimental conditions during the pulling-up process. The process produced a capillary force, i.e., a gas–liquid interfacial tension, to push the particles into the recessed patterns on the substrate. In most cases, the selectively depositing particles within the recessed patterns self-organically formed the closest packing structures. However, a special phenomenon, cubic packing structures of the particles, was observed when using square patterns with a few times larger side-length than the particle diameters. Several particle packing structures within different-sized square patterns were demonstrated, and the relationship between the particle packing structures and square pattern sizes were discussed.

Keywords: Polystyrene particle; Self-assembly; Capillary force; Silicon-microfabricated substrate; Hexagonal closest packing; Cubic packing

1. Introduction

Recently, there is great interest in arrangement of micrometer- or nanometer-sized particles on a substrate because of their potential use in sensors, magnetic storage media, templates for nanostructure formation, and photonic bandgap crystals [1,2]. Particle arrangements are classified into the following four categories: “colloidal crystal”, “monolayer-particle film”, “particle chain”, and “particle array dot” formation (three-, two-, one-, and zero-dimensional particle arrangements, respectively). Several approaches have been widely studied to arrange microparticles or nanoparticles on substrates, including ink-jet printing, nanoprobe lithography, micro-contact printing, and nanoparticle arrangement using the patterning substrate as a template [3]. Among them, the template-assisted procedures using microfabricated recessed pattern substrates are simple and feasible without any special equipment and techniques. In our previous report, the polymer nanoparticles array dot, the zero-dimensional particle arrangement, was realized using silicon-microfabricated substrates and a simple dipping and pulling-up process [4]. Recently, we applied the same technique to the two-dimensional particle arrangement.

The two-dimensional monolayer-particle films have been widely reported including its potential application as a mask for lithography [5–8]. In these studies, the monolayer-particle film was formed on the flat surface substrate; therefore, it was difficult to prepare the two-dimensional monolayer-particle film with the desired size. In addition, the structure of the monolayer-particle film is fixed only on one specific structure, spontaneously forming a hexagonal closest packing structure. We used the microfabricated silicon substrates as the templates for the monolayer-particle film to obtain the films with the desired sizes and structures. In this paper, submicrometer-sized polystyrene particle packings within various silicon micrometer-sized recessed patterns and their packing structures in the patterns are described.
2. Experiments

2.1. Materials

Polystyrene particles with the diameters of 115 ± 10, 450 ± 25, and 1000 ± 50 nm were prepared by the emulsifier-free emulsion polymerization in water using the styrene monomer, sodium p-styrenesulfonate as a dispersion stabilizer, divinylbenzene as a cross-linker, and potassium persulfate as a water-soluble polymerization initiator. The particle sizes were changed by tuning the amount of the dispersion stabilizer [9].

Silicon substrates with micrometer-sized recessed patterns were fabricated by the electron beam- or photolithography and the etching of the SiO$_2$ layer. The microfabricated substrate has square, equilateral triangular, or circular recessed areas (patterns) with micrometer-scale side-lengths or diameters, and nanometer-scale depths at the lattice point with a 5–20 μm interval. A series of silicon-microfabricated substrates with different square pattern sizes (side-length: 0.85, 1.20, 1.37, 1.80, 2.10, 2.25, 2.70, 3.20, and 5.00 μm; depth: 110 nm) were prepared. The substrates with equilateral triangle patterns (side-length: 1.80, 2.25, 2.70, and 3.20 μm; depth: 110 nm) and circular patterns (diameter: 1.80, 2.25, 2.70, and 3.20 μm, depth: 110 nm) were also prepared. The surface of these substrates is characterized by two different areas; i.e., the hydrophilic SiO$_2$ area, which covers the entire surface, and the hydrophobic Si area at the bottom of the recessed patterns.

2.2. Selective deposition of polystyrene particles using a dipping and pulling-up process

A kind of template-assisted procedure, a dipping and pulling-up process of a microfabricated substrate from a polystyrene particle aqueous suspension using simple handmade equipment, was used as the method for the particle arrangement. Our simple equipment consists of a holder with a small clip to hold the substrate at the pulling-up particle arrangement. Our simple equipment consists of a handmade equipment, was used as the method for the polystyrene particle aqueous suspension using simple pulling-up process of a microfabricated substrate from a dipping and pulling-up process.

Selecting deposition of polystyrene particles using a hydrophobic Si area at the bottom of the recessed patterns.

Pattern size, particle suspension concentration, pulling-up speed, and pulling-up angle of the substrate surface versus the aqueous suspension surface) were examined based on the results of our previous similar experiments [4]. The arrangements of the polymer particles on the silicon-microfabricated substrates were observed with a scanning electron microscope (SEM, Keyence VE-7800) and a field-emission scanning electron microscope (FE-SEM, Hitachi S-4200SE).

3. Results and discussion

3.1. Packing of submicrometer-sized polystyrene particles within silicon-microfabricated patterns

The silicon-microfabricated substrates, which have micrometer-sized square, equilateral triangular, or circular recessed patterns fabricated by the microfabrication procedure, were used as the template for the polystyrene particle arrangement. The microfabricated silicon substrate was dipped into the aqueous suspension of the polystyrene particles, and then it was slowly pulled up at both a constant speed and a constant angle using the pulling-up equipment. The polystyrene particles were self-organically deposited and formed particle packing structures within the patterns on the substrate by a capillary force effect in a meniscus region, where the capillary force (the gas–liquid interfacial tension between the hydrophilic SiO$_2$ surface and water) works to push the particles into the recessed patterns and to sweep extra particles from the SiO$_2$ surface (area outside the patterns).

The selectivity of the particle deposition in the patterns, which is defined as the ratio of the number of deposited particles within the patterns versus the total number of particles including the particles deposited in the area outside the patterns, were subjected to the following experimental conditions: particle size, pattern size, particle suspension concentration, pulling-up speed, and pulling-up angle. The suspension concentration and the pulling-up speed were first examined while keeping the other factors constant (particle diameter: 450 ± 25 nm, side-length of square patterns: 4.0 μm, side-length of equilateral triangular patterns: 3.2 μm, diameter of circular patterns: 3.2 μm, and pulling-up angle: 135°). The combination of the pulling-up speed of 10 μm/s and the suspension concentration of 0.5 wt% produced an almost 100% selective deposition of the polystyrene particles within the recessed patterns. Fig. 2 is an SEM image of the particle packing within the square, equilateral triangular, and circular patterns. Each pattern was filled with polystyrene particles without any defects. This almost 100% selective deposition of the polystyrene particles within the patterns were observed over the wide area of 30 × 40 μm on the same substrate.

The particle packing structure in the larger square pattern was minutely observed by the FE-SEM (Fig. 3). The submicrometer-sized polystyrene particles were deposited within the patterns with a hexagonal closest packing...
structure bordering on the surrounding particles. The hexagonal closest packing structure in a pattern occurred due to the particle self-assembly to form the most stable structures as well as the usual monolayer-particle films.

### 3.2. Effects of particle and box sizes

The size effects of the polystyrene particle and the microfabricated pattern on the particle packing in the square patterns were examined. First, the particle sizes were changed to determine the particle size effect on the particle packing. The hexagonal closest packing with the larger particles (diameter: \(1000 \pm 50 \text{ nm}\)) in the square patterns (side-length: \(5.0 \mu\text{m}\)) was achieved under the same conditions as that of the \(450 \pm 25 \text{ nm}\) diameter particles. In the case with smaller particles (diameter: \(115 \pm 10 \text{ nm}\)), the difficulty in the selective deposition of particles within the patterns increased due to the influence of Brownian movement; however, the particle packing structures were same as that of the larger particles, i.e., smaller particles also formed the hexagonal closest packing structures in the patterns. On the other hand, the effect of the box size appeared when using the substrates fabricated with the square patterns having a side-length of 0.85, 1.15, 1.37, 1.58, 1.80, 2.10, and 2.25 \(\mu\text{m}\) (2–5-time larger than the particle diameter: \(450 \pm 25 \text{ nm}\)). Among them, for the substrate bearing the square pattern with a 1.15 or 1.58 \(\mu\text{m}\) side-length (2.5 or 3.5 times larger side-length than the particle diameter of \(450 \pm 25 \text{ nm}\)), neither a closest packing in a square pattern nor a selective deposition in the patterns occurred (Fig. 4). Overflows of the particles were observed in these cases, because the square pattern did not bear an adequate side-length, i.e., the exact multiple of the particle size. The selective deposition of particles within the equilateral triangular patterns (side-length: 1.80, 2.25, and 2.70 \(\mu\text{m}\); depth: 110 nm) and the circular patterns (diameter: 1.80, 2.25, and 2.70 \(\mu\text{m}\); depth: 110 nm) were successful because they had 4-, 5-, and 6-times larger side-lengths (or diameter) than the particle sizes (diameter: \(450 \pm 25 \text{ nm}\)).

The hexagonal closest packing similar to the image in Fig. 3 was observed for the combination of the 450 nm particles and the 2.25 \(\mu\text{m}\) side-length square pattern substrate (5 times larger than the particle size). However, the particle packing structure was dramatically switched from the hexagonal closest packing to the cubic packing structure for the 2- and 3-times larger square patterns. The 450 nm diameter particle in the 1.8 \(\mu\text{m}\) side-length square

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**Fig. 2.** SEM images of the polystyrene particles (diameter: 450±25 nm) packing within the (a) square patterns (side-length: 4.0 \(\mu\text{m}\)), (b) equilateral triangular patterns (side-length: 3.2 \(\mu\text{m}\)), and (c) circular patterns (diameter: 3.2 \(\mu\text{m}\)) on the silicon-microfabricated substrates.

**Fig. 3.** FE-SEM image of the hexagonal closest packing of polystyrene particles (diameter: 450±25 nm) within a square pattern (side-length: 5.0 \(\mu\text{m}\)) on the silicon-microfabricated substrate.

**Fig. 4.** FE-SEM image of deposited polystyrene particles (diameter: 450±25 nm) on the silicon square pattern (side-length: 1.58 \(\mu\text{m}\)) substrate.
pattern (4 times larger than the particle size) formed a mixture of the cubic and hexagonal closest packing structures (Fig. 5).

3.3. Mechanism of particle packing within square patterns

We now discuss the particle packing process within the square patterns in order to understand the previously described interesting results. The interaction between a particle and a substrate, and the interaction among particles are effective for the selective deposition of particles and the formation of packing structures within the patterns. Hydrophobic polystyrene particles dispersed in aqueous media are liable to adsorb on a substrate especially at the edge of the patterns and to aggregate one another to reduce the surface potential of the particle. The particle packing mechanism is regarded to include the following three steps: (1) the first particle deposition, (2) the following particle deposition, and (3) restructure of particle packing structure. The first particle is considered to deposit at the square pattern corner selectively because the particle deposited at the corner becomes stable due to reduction of the surface potential of the particle by coming in contact with the pattern edges through multipoints (step 1). The following particles deposit one after another into the square pattern, especially (a) at other corners, (b) on the edges of the square pattern, and (c) next to the first particle through a hydrophobic interaction among particles (step 2). The particles gradually deposit into the patterns from the circumferences to the center of the square pattern. After almost all the particles are deposited in the pattern, the particle aggregate will be restructured into the most stable packing structure (step 3). In this step, the particles remove from the pattern edges to form a more stable hexagonal closest structure because the multipoint interaction among the particles is stronger than the interaction between the particle and the edges. Although the contact point between the particles and the edges reduced with this restructure, the particles with the hexagonal closest packing structures must be in contact with more particles than the particles with cubic packing structures. However, the restructure of particles into the hexagonal structures were not observed in “small” size square patterns, which had 2- or 3-times larger side-length than the particle size. Instead of the hexagonal closest packing structures in the “large” patterns, cubic packing structures were formed in the “small” patterns. The border of the “small” and “large” pattern sizes is located at the square patterns with 4-times larger side-length than the particle size. In the “small” patterns, interaction between particles and pattern edges are considered to be dominant to prevail over the interaction among particles since more particles in the “small” patterns are in contact with the pattern edges than that in the “large” patterns. Therefore, the interaction between the particle and the substrate significantly prevents the restructure of the particles in the “small” patterns (Fig. 6).

Cubic packing of the particles is a special phenomenon and is not observed in the normal particle assembly. The
monolayer-particle film bearing the cubic packing structures has potential applications such as a mask-bearing exposure sites at the lattice points. A cubic-structured monolayer-particle film with a wide area is now being constructed using a silicon patterning substrate with micrometer-sized grille-like low protuberances.

4. Conclusion

The packings of submicrometer-sized polystyrene particles within micrometer-sized recessed patterns on silicon substrates were achieved using a simple template-assisted procedure. A special phenomenon, the cubic packing of particles, was observed when using a square pattern substrate with 2- or 3-times larger side-length than the particle diameters. The particle packing formation mechanism is considered as follows. In the “large”-sized square patterns, particles aggregate to form hexagonal closest structures because the multipoint interaction between the particles is stronger than that between the particle and the edge of the square pattern. On the other hand, particles in the “small”-sized square patterns form cubic packing structures due to the strong interaction between the particles and the edge of the square pattern. This cubic-structured monolayer-particle film would have potential applications, such as a mask-bearing exposure sites at lattice points.

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