

Selective deposition of polystyrene nanoparticles in a nanoetchpit array on a silicon substrate†

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Nanometer-sized polystyrene particles were selectively deposited by interfacial tension in nanometer-sized etchpit arrays made on a silicon substrate.

Recently, there has been great interest in the arrangement of nanoparticles (nanometer-sized homogeneous particles with a diameter from a few nanometers to sub-micrometers) on a substrate.¹ Several approaches have been studied, including laser manipulation,² ink-jet printing,³ nanoprobe lithography,⁴ and nanoparticle arrangement using the substrate as a template.^{5,6} Among these, the template-assisted procedures are simple and feasible without any special equipments and techniques. There have been reports of the deposition of a micrometer-sized particle upon a similar-sized pit which was recessively formed on a substrate as a kind of template,⁵ and the coagulation of numerous nanoparticles into the micromold structure on a substrate.⁶ However, to our knowledge, an array-like arrangement of nanometer-sized particles on a substrate has never been reported. This communication describes, for the first time, the selective deposition of polystyrene nanoparticles in nano-etchpits, *i.e.*, pits with a diameter of *ca.* 100 nm formed by a wet-etching procedure on a silicon substrate.

One of the coauthors (I. O.) has developed silicon nano-etchpit-array (NEPA) substrates by a microfabrication technique.⁷ Fig. 1 shows atomic force microscopic (AFM) images of the typical NEPA substrate used in this paper, which possesses cylindrical nano-etchpits with a constant interval on lattice points of the silicon substrate.⁸ On the other hand, crosslinked and monodispersed (<10%) polystyrene nanoparticles with diameters = 35, 50, 80, 115, and 170 nm and volume density = 1.03 were prepared by emulsion polymerization using sodium *n*-dodecyl sulfate as an emulsifier.

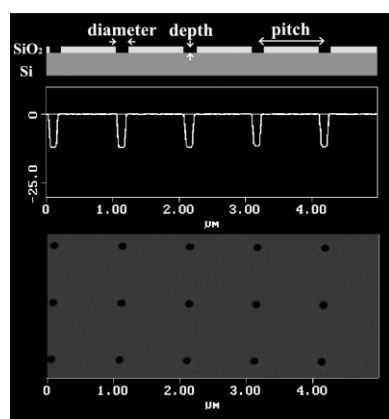


Fig. 1 AFM image (bottom), cross section image (middle) and cross sectional illustration (upper) of a typical silicon NEPA substrate with etchpits of 100 nm diameter, 12 nm depth and 1 μm pitch.

† Electronic supplementary information (ESI) available: selective deposition of polystyrene particles with smaller diameter. See <http://www.rsc.org/suppdata/cc/b3/b315816k/>

The NEPA substrate was dipped in the aqueous suspension (30 ml) of the polystyrene nanoparticles, and then it was pulled up slowly at both a constant speed and a constant angle (θ) of the substrate surface *versus* the aqueous suspension surface.⁹ This process provides a capillary force, *i.e.*, an interfacial tension between the hydrophilic SiO₂ surface and water, to push the nanoparticle into the etchpit of the substrate.

The first issue for depositing one particle in one etchpit was the relative size of the particle (guest) diameter (d) and the etchpit (host) diameter (D). Multiple particles were deposited in each etchpit for $D/d > 2$. Fig. 2 shows an example of the deposition of four or five particles ($d = 115 \pm 10$ nm) in one etchpit ($D = 300 \pm 15$ nm, depth = 100 ± 5 nm). This result agreed with the calculated values;⁵ four particles in one etchpit for $2.41 < D/d < 2.70$ and five for $2.70 < D/d < 3.00$. A high deposition yield of one particle in each etchpit was observed for the combination of $d = 170$ nm and $D = 130$ nm where the particle diameter was slightly larger than the etchpit diameter. Here, the yield is defined as the ratio of the number of deposited particles in the etchpit *versus* the total number of the particles. The above combination of particle and etchpit diameters was used in the following experiment.¹⁰

The angle, θ , was the second issue for depositing the nanoparticles in a high yield. As a result of changing θ from 90° to 150°, $\theta = 135^\circ$ was selected as the best angle to deposit the nanoparticles in etchpits. It turned out that the larger angle was desirable for the selective deposition of nanoparticles in etchpits within $90^\circ < \theta < 135^\circ$. However, the particles often remained on the SiO₂ surface and not in the etchpits (yield *ca.* 30%) above the pulling-up angle of 135°.

Other issues were the particle suspension concentration and the pulling-up speed which were related to each other. We found two optimal conditions for the fast pulling up from a low-particle concentration suspension ($100 \mu\text{m s}^{-1}$ and 0.1 wt%, respectively) and the slow speed from a high concentration one ($20 \mu\text{m s}^{-1}$ and 0.2 wt%, respectively). Fig. 3 demonstrates the selective and quantitative depositions of the polystyrene nanoparticles (without any defects). A 100%-yield deposition was realized at least in a $20 \times 15 \mu\text{m}^2$ region on the substrate with reproducibility.

Hereinafter we discuss the forces which work upon the deposition process of the nanoparticle in the etchpit. First, the surface of the SiO₂ substrate is characterized to be hydrophilic which was estimated by measuring the contact angle of a water droplet to be 45°. On the other hand, the inside surface of the etchpit is presumed to be hydrophobic (contact angle = 84°). The surface

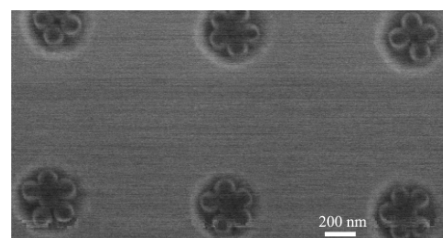


Fig. 2 SEM image of multiple polystyrene nanoparticles (diameter = 115 ± 10 nm) deposited in one etchpit (diameter = 300 ± 15 nm).

of the polystyrene nanoparticle is covered with the surfactant sodium *n*-dodecyl sulfate and is relatively hydrophilic, which was supported by measuring the contact angle (38°) of a water droplet on a polystyrene nanoparticle film prepared by a spin-coating method. Other polystyrene nanoparticles such as Polybead (Polysciences Inc.) bearing amino or carboxyl groups were also deposited selectively in the etchpits. Therefore, an interaction between the hydrophilic particle surface and the hydrophobic etchpit is considered not to be predominant for the selective deposit of a particle into the etchpit.¹¹

The following two forces are expected to deposit the nanoparticle into the etchpit: (i) a capillary force, *i.e.*, the surface tension ($\sim 10^{-8}$ N) that acted upon the particle partially immersed in an aqueous layer just before the deposition;¹² and (ii) a frictional force (F_d , $\sim 10^{-8}$ N) between the substrate and the particle. The surface tension of (i) is divided into a parallel force (F_{\parallel}) versus the substrate surface and a perpendicular force (F_{\perp}) which works on the particle toward the substrate surface.¹³ Under the experimental conditions of Fig. 3(b), the two forces were calculated to be $F_{\parallel} = 1.2 \times 10^{-8}$ N and $F_{\perp} = 2.8 \times 10^{-8}$ N, respectively.¹⁴ The frictional force, which works parallel but reversely in the progressive direction of water on the deposition process, was calculated to be $F_d = 1.0 \times 10^{-8}$ N.¹⁵ After summing them up, the perpendicular force ($F_{\perp} \sim 10^{-8}$ N) was considered to be the main force that pushes the particle into the etchpit.

In conclusion, the selective deposition of polystyrene nanoparticles into array-like made nano-etchpits was realized by a simple dipping and pulling-up process. This process is applicable for the arrangement of various functional nanoparticles.

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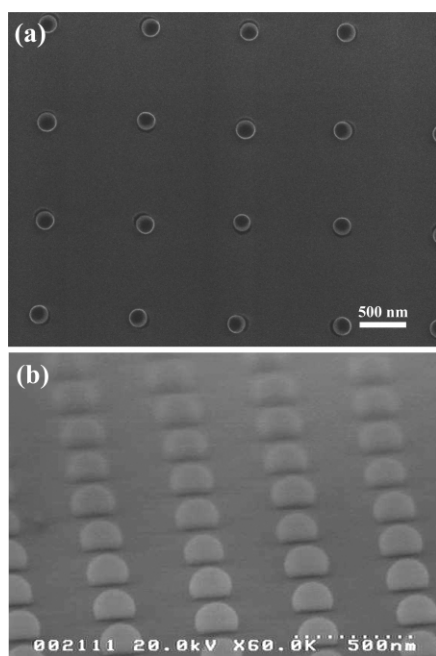


Fig. 3 SEM images of selective deposition of the polystyrene nanoparticle (diameter = 170 ± 15 nm) in the etchpit (diameter = 130 ± 10 nm, depth = 50 ± 5 nm) prepared by pulling-up the substrate from the particle aqueous suspension under the following conditions: (a) polystyrene concentration = 0.2 wt %, pitch of etchpits = $1 \mu\text{m}$, pulling-up speed = $20 \mu\text{m s}^{-1}$, and pulling-up angle = 135° , (b) polystyrene concentration = 0.1 wt %, pitch of etchpits = 500 nm , pulling-up speed = $100 \mu\text{m s}^{-1}$, and pulling-up angle = 135° .

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- The SiO_2 surface of the 10 mm square silicon substrate was coated with a photoresist resin (Zep-520, Nihon Zeon Co.), which was patterned by electron beam exposure (Hitachi modified S-4200SE SEM combined with Tokyo Technology's lithography system). After etching the oxide layer with aqueous HF solution through the patterning mask, the substrate was cleaned by oxygen plasma etching and chemical washing. Nine kinds of NEPA substrates were prepared: etchpit diameter = 100 ± 10 , 130 ± 10 , and 300 ± 15 nm; depth of etchpit corresponding to the diameters = 12, 50, and 100 nm, respectively; pitch of the etchpit = 0.5, 1.0, and $2.0 \mu\text{m}$.
- This dipping and pulling-up process was carried out with simple equipment, which consisted of a holder with a small clip to hold the substrate, a motor which moves the holder with a constant speed, and a computer to control the pulling-up speed and the angle. The pulling up speed and the angle were set from 0.1 to $100 \mu\text{m s}^{-1}$ and from 90 to 180° , respectively.
- Selective deposition of the polystyrene particles with a smaller diameter was also achieved. See ESI†.
- Other forces such as gravitation, buoyancy, Coulomb's force, and van der Waals force should be less significant ($< 10^{-14}$ N) in this experiment.
- Polystyrene nanoparticles dispersed in organic solvents such as chloroform and THF were not deposited in the etchpits because their surface tension was very small. Particles in methanol were slightly deposited in the etchpits.
- A lateral motion of the particles was negligible in the well-dispersed and dilute suspension of this experiment.
- The situation was examined when one particle was just half-immersed in an aqueous layer, where the surface tension is expected to be largest, and any Brown movement and interaction among the particles could be ignored. The surface tension caused between the water and the particle surface, and the force direction was estimated by contact angle measurement. The sum of the surface tensions, which was calculated using the circumference of the particle under the conditions of Fig. 3(b), was *ca.* 3.9×10^{-8} N based on the air–water interfacial tension of $7.28 \times 10^{-2} \text{ N m}^{-1}$ (at 20°C). The force was divided into parallel and perpendicular components to the substrate, by considering the slope of the aqueous layer caused by the contact angle between the substrate and water. The contact angles were 30, 27, 23, and 15° for the substrate pulling-up angles of 90, 120, 135, and 150° , respectively, and the parallel direction force for a particle to move forward was calculated to be $F_{\parallel} = 1.5 \times 10^{-8}$, 1.4×10^{-8} , 1.2×10^{-8} , and 7.9×10^{-9} N, respectively. On the other hand, the perpendicular component, which works to deposit a particle in an etchpit, was $F_{\perp} = 2.5 \times 10^{-8}$, 2.7×10^{-8} , 2.8×10^{-8} , and 3.0×10^{-8} N, respectively, for each pulling-up angle.
- The frictional force F_d [N] of an object in a fluid is provided by Stokes' law for a laminar flow: $F_d = (24 \mu / \rho v d_p)(\rho v^2 / 2)(\pi d_p^2 / 4) r$, where μ , ρ , v , d_p , and r are the viscosity coefficient of water [Pa s], the density of water [kg m^{-3}], the velocity of water [m s^{-1}], particle diameter [m], and the ratio of a particle cross section area immersed in an aqueous layer vs. the largest cross-sectional area, respectively. The frictional force was calculated to be $F_d = 1.0 \times 10^{-8}$ N under the conditions of Fig. 3(b).