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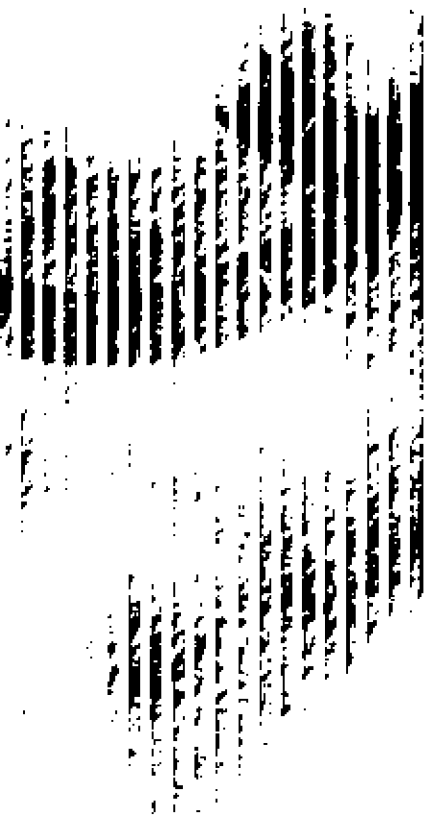

Self-Assembly of Fine Particles on Patterned Wettability in Dip Coating and Its Scale Extension with Contact Printing*

Yoshihito KANAMORI**, Arata KANEKO**, Nobuyuki MORONUKI** and Takafumi KUBO**

**Graduate school of System Design, Tokyo Metropolitan University, 6-6, Asahigaoka, Hino, Tokyo, 191-0065, Japan

E-mail: kaneko-arata@tmu.ac.jp

Abstract

This study demonstrates the application of dip coating to self-assembly of fine particles on a substrate that is covered with line-and-space pattern of hydrophilic (SiO_2) and hydrophobic materials (OTS). The pattern was fabricated on a substrate by lithography first. The substrates were drawn up from the water-based suspension in which particles were dispersed and the particles self-assembled on the hydrophilic region only forming the packed-structure. Then, contact printing was applied for the patterning to extend the scale. The scale was extended up to 10mm x 10mm while keeping the self-assemble performance.

Key words: Particle, Self-Assembly, Wettability, Dip Coating, Contact Printing

1. Introduction

Assembly of micro/nano-particles allows new functional devices such as microlens[1], biosensor[2-3], etching mask[4], and photonic crystal[5-8]. So far, various assembly technique were tried, e.g., laser trapping[9], SPM manipulation[10], and dip coating[11-13]. However, any assembly technique that compromises various requirements such as accuracy, productivity, and spatial selectivity has not been established. It is well known that dip coating process, drawing-up a substrate from suspension in which particles are dispersed, enables the self-assemble of particles on a hydrophilic substrate[11-13]. The particles autonomously pack in hexagonal due to the capillary forces among them as the evaporation of liquid in suspension. This method can provide an easier way and higher productivity to assemble particles comparing with the other technique, but it is difficult to assemble particles selectively on specific position.

It has been reported that pure water selectively wet and/or spread on the specially patterned substrate with an array of hydrophilic and hydrophobic materials[14]. Dip coating with hydrophilic/hydrophobic pattern can locate particles on desired region with high productivity. The hydrophilic/hydrophobic pattern was fabricated by Electron beam (EB) lithography method and could be assembled particle on this pattern[14]. But the pattern size is limited because the time required for lithography is proportional to the size. Therefore, it is difficult to assemble particle on large area. Contact printing technique has been applied for various patterning[15-21]. This process is effective especially in the case of large scale patterning because the patterning can be carried out in parallel over the mold size. However, it is not necessarily applied for hydrophilic/hydrophobic patterning and optimum conditions have not been made clear.

This paper firstly demonstrates self-assembly of fine particles by dip coating using hydrophilic/hydrophobic patterned substrate prepared with EB-lithography. Then, contact

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printing is applied to optimize patterning process for scale extension of self-assembly area.

2. Self-assembly mechanism

Figure 1 shows the schematic illustration of dip coating with hydrophilic/hydrophobic pattern[14]. Patterned substrate is dipped into the suspension in which particles are dispersed and then draw up at constant speed V and angle φ. The suspension locally spreads on hydrophilic region with the help of capillary force. According with the evaporation of solution particles self-assembled forming hexagonally packed-structure due to the meniscus forces among them.

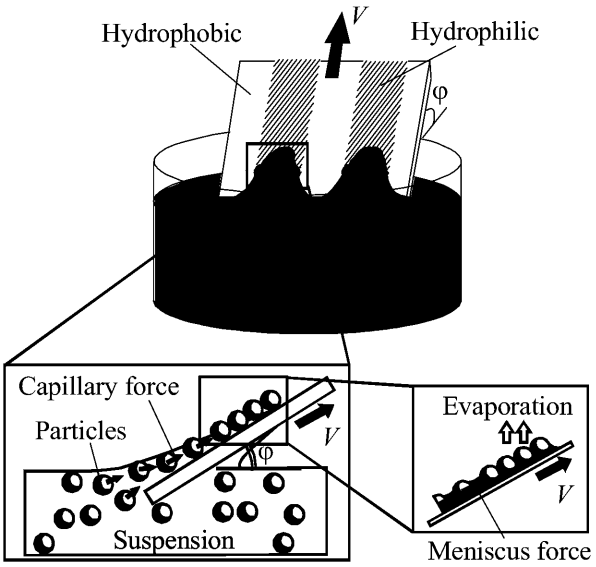


Fig. 1 Schematic illustration of self-assembly mechanism on hydrophilic/hydrophobic-pattern.

3. Self-assembly on substrates fabricated by EB-lithography

3.1 Substrate preparation

Figure 2 shows the process steps of EB-lithography patterning[14]. Firstly, Si (100) wafer was soaked in H_2SO_4 : H_2O_2 = 3 : 1 solution kept at 70 degrees for 2 hours to form thin SiO_2 layer. Then, the octadecyltrichlorosilane (OTS) self-assembled monolayer (OTS-SAM) was deposited by dipping in OTS-toluene solution (1 wt%) for 2h, and the substrate was soaked in H_2SO_4 to clean up excess OTS. OTS reacts well with hydroxyl groups, including the environmental water vapor. Therefore, this process was carried out in a glove box purged with dry N_2 gas. Then, electron beams were irradiated to remove OTS with specified pattern. The dose amount was set at 4000 $\mu C/cm_2$. Finally, Irradiated OTS was removed and SiO_2 layer was produced in H_2SO_4-H_2O_2 solution.

Figure 3 shows the atomic force microscope (AFM) image and contact angle that was measured on wider samples. Step height between OTS and SiO_2 was 1.4 nm, which corresponded to OTS molecular length and thus this layer is confirmed as monolayer OTS (OTS-SAM). The contact angle of SiO_2 region θ_{SiO2} was 34 degrees and that of OTS region θ_{OTS} was 108 degrees respectively for pure water of 1 μl. The OTS region had enough hydrophobic property because the contact angle was larger than 90 degrees. However, the SiO_2 region had weak hydrophilic property because the contact angle was rather large. Ideally, the contact angle of SiO_2 is less than 10 degrees. These properties may affect the self-assembly process.

The patterned area was 1 mm x 1 mm, and it took for 2 hours. EB-lithography is convenient for small lot fabrication because no glass mask is necessary, but, it is difficult to adopt large scale fabrication because it takes long time.

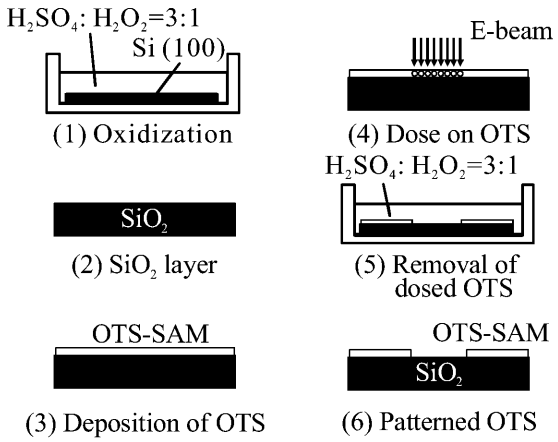


Fig. 2 Patterning-process step by EB-lithography.

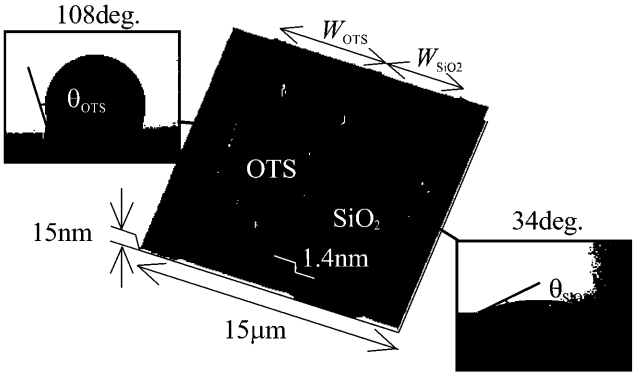


Fig. 3 AFM image and contact angle on typical substrate fabricated by EB-lithography.

3.2 Setup for dip-coating

Figure 4 shows the schematic illustration of the experimental setup. The system consists of an inchworm actuator, a rotation stage, and a reservoir. The inchworm-type linear stage draw up a substrate at required drawing speed V. The rotational stage was used to set the drawing angle φ ranging from 0 to 90 degrees. The reservoir was filled with a suspension in which polystyrene particles of 1 μm in diameter disperses in pure water at 1 % concentration. The reservoir size was ϕ 20 x 5 mm. This system is set in a clean room in which temperature and humidity are kept at 20 centigrade and 50 % respectively.

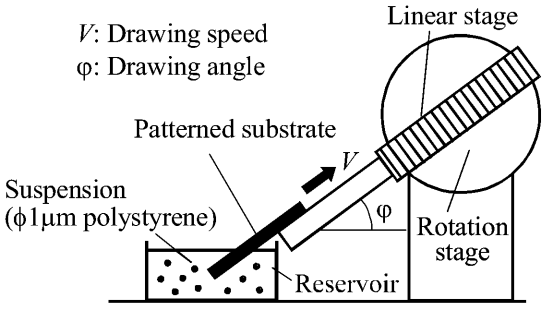


Fig. 4 Experimental setup.

3.3 Results and discussion

The patterned substrate was drawn up from the suspension at speed V = 4 μm/s and angle φ = 30 degrees. The geometry of hydrophilic/hydrophobic pattern used line and

space at W_{OTS} = 50 μm and W_{SiO2} = 50 μm. Figure 5 shows the scanning electron microscope (SEM) images of self-assembled particles on the substrate. The patterning field size was 1 mm x 1 mm and smaller part within it was observed. The particles were assembled only on the SiO_2 region, and they did not remain on the OTS region. Assembled particles were hexagonally packed in monolayer. Thus, this result is satisfactory though some defects just like cracks can be seen. The difference of the brightness on the substrate shows the difference of the surface material. It was found that the width of the assembled region was smaller than that of SiO_2 region 50 μm. This is because the local spread on the SiO_2 region took complicated shape and the final assembled width is always smaller than that of the pattern. If an accurate size is required, the pattern width should be larger to compensate this effect.

The problem of EB-lithography process is only the pattern size. As described before, EB-lithography requires long time. Therefore, particles cannot assemble large-scale region.

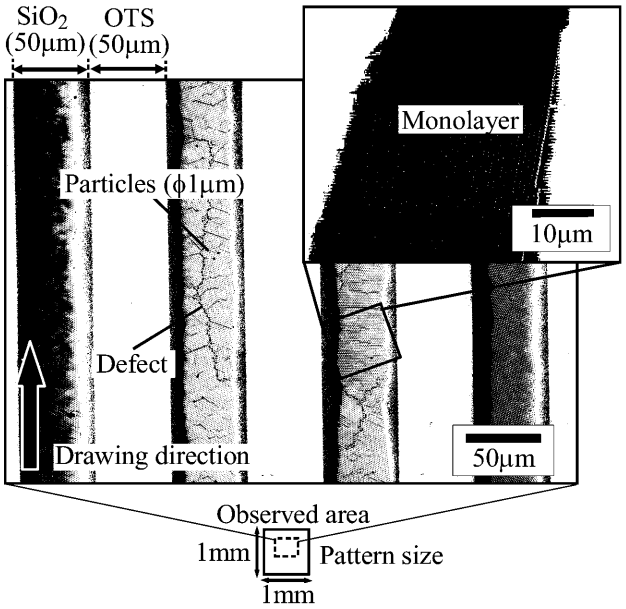


Fig. 5 Self-assembled particles on patterned substrate fabricated by EB-lithography (W_{SiO2} = 50μm, W_{OTS} = 50μm).

4. Scale extension of assembly area using contact printing

4.1 Preparation of the substrates

Contact printing has been applied for various material transfers and their scale extension[15-21]. Fabrication of hydrophilic/hydrophobic pattern with contact printing can, of course, extend its scale. However, basic properties have not been made clear. Thus, the printing process itself should be discussed before the self-assembly. Figure 6 shows the process steps of fabricating OTS and SiO_2 patterned substrate by contact printing. Firstly, the master mold with proper micro-structure was prepared with photolithography. Then, polydimethylsiloxane (PDMS) with 10 wt% of curing agent was cast onto the mold, cured at the temperature of 70 degrees for 2h, then, the PDMS was peeled off from the mold. The PDMS casting was inked with OTS. Finally, the inked OTS was printed on the SiO_2 substrate. A contact pressure was applied during a period of time of which effect is discussed later. The pressure was kept at constant applying only the own weight of the PDMS casting.

The substrate was covered with SiO_2 layer formed by soaking in H_2SO_4 : H_2O_2 = 3 : 1 solution for 2 h at temperature of 70 degrees. Just same with EB-lithography, OTS reacts

quickly with hydroxyl groups. Contact printing was carried out in a glove box purged with N_2 gas.

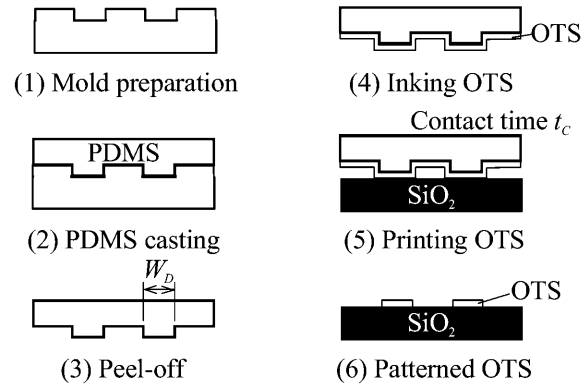


Fig. 6 Process step for OTS contact print.

It was found that the contact time in the printing process affect the properties of transferred OTS, though the OTS reacts with SiO_2 in a short time theoretically. Figure 7 shows the effect of contact time on the contact angle of OTS region θ_{OTS} and pattern width of OTS W_{OTS} (See Fig. 3). With the increase in contact time t_C, both of θ_{OTS} and W_{OTS} became larger. It is considered that the contact time determined the number of transferred OTS molecules and the increase of W_{OTS} was caused by the elastic deformation of the mold. Thus, the contact time should be determined to obtain the desired θ_{OTS} and then the initial mold shape (W_D) should be designed to compensate the expected deformation to obtain desired W_{OTS} based on these preliminary experiments.

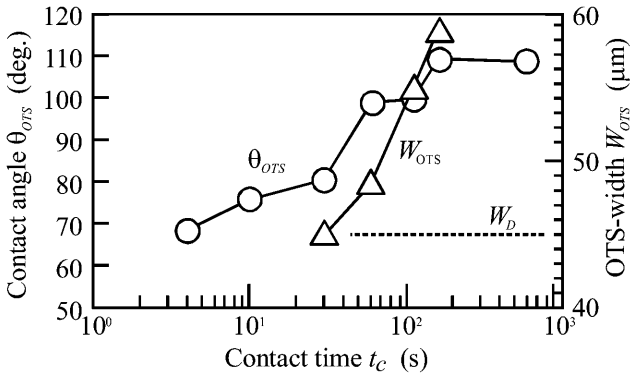


Fig. 7 Effect of contact time t_C on the contact angle θ_{OTS} and pattern width W_{OTS}.

Figure 8 shows the change in the contact angle after contact print. The contact angle on OTS region is stable and no change is observed along time. However, the contact angle on SiO_2 region increased with time up to 60 degree after 1000 hours. The droplet shapes are also shown in the figure. The effect of this change will not be neglected because the difference between the hydrophobic and hydrophilic property causes the location selective self-assemble discussed in this paper. From this results, it was found that the assemble process should be completed before 24 hours after the contact print. This condition is not so critical because it does not take long time for the assembling process.

4.2 Assembly results and discussion

The patterned substrate was draw up from the suspension at drawing speed $V = 8$ μm/s and angle $\varphi = 30$ degrees. The setup and suspension is same with the former experiments.

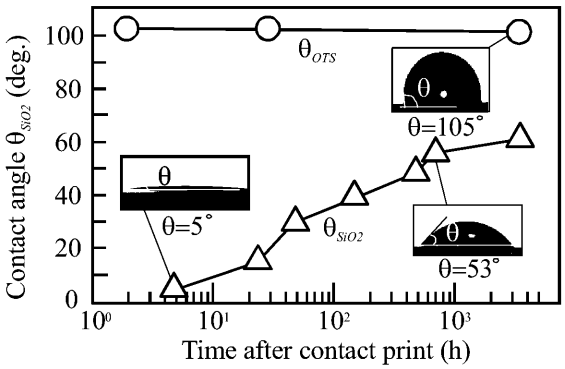


Fig. 8 Contact angle for pure water plotted against time after contact print.

The design of hydrophilic/hydrophobic pattern was line-and-space with W_{OTS} 45 μm and W_{SiO2} 50 μm. The contact angle of each region was 98 degrees for OTS and 5 degrees for SiO_2 region respectively. The contact angle of OTS layer is smaller than that of the former experiments. The reason might be the imperfect structure of OTS. In the former experiments, the OTS molecule has confirmed to be grown in monolayer based on the observation with AFM as shown in Fig. 3.

It was found that the particles do not assemble on the substrate in one time drawing-up and iterated drawing-up was necessary to improve the coverage. Figure 9 shows the effect of drawing times on the coverage. The coverage ε is defined as P_2/P_1, where P_1 and P_2 are respectively the area of SiO_2 region and the covered area with particles on the SiO_2. The maximum ε is limited up to 85 % because opening area remained among particles. As shown in the figure, the coverage is just 10 % at the first drawing. The coverage, however, became larger than 70 % after 15 times drawing. Considering this coverage, the efficiency for self-assembly increased with iteration times of drawing. It can be considered that the difference in drawing speed also affects this coverage and its change in iteration times.

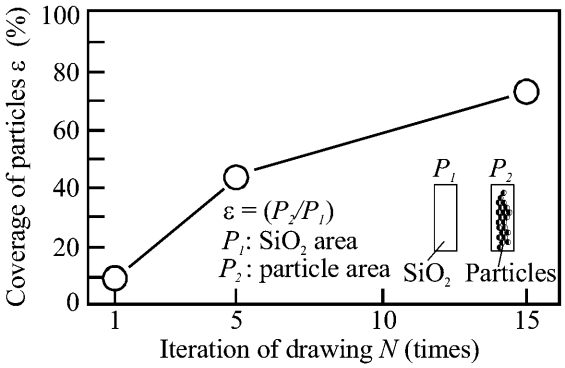


Fig. 9 The effect of drawing time on coverage of particles.

Figure 10 shows the observation results with laser microscope and SEM images of self-assembled particles after one time drawing. Hatching lines are superimposed on the image to indicate the location of SiO_2 regions. The result is rather different from the intention, because the particles did not assemble on most of the SiO_2 regions, where the particles should selectively assemble. Particles assembled on just two regions on these patterns. In addition, the layer is not monolayer but multilayered as shown in the magnified view in right upper of the figure. Many defects, line defects just like cracks or point defects just like vacancies, are observed in the layered region. Thus, the assembly was imperfect from the various viewpoints.

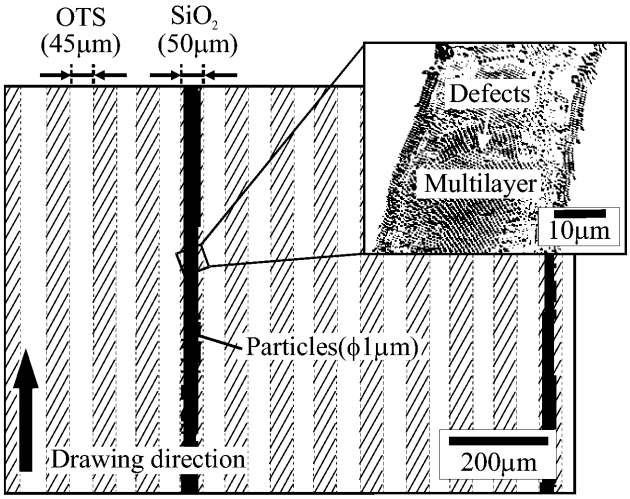


Fig. 10 Assembled result after first drawing.

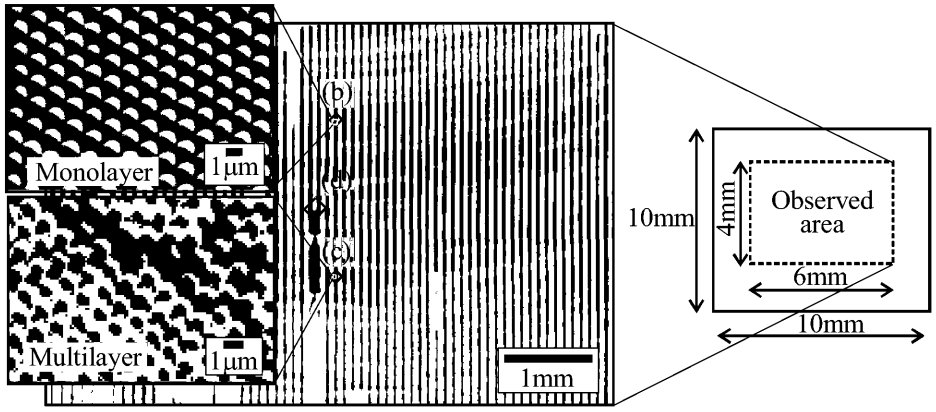
Figure 11 shows the observation results with confocal type laser microscope and SEM images that show the self-assembled particles on large-scale observation (6 mm x 4 mm) on the assembled area of 10 mm x 10 mm. The dark stripe pattern denotes the assembled particles as shown in the magnified image in the upper left of the figure. The assembled particles are represented as dark and bright grey-colored regions in the large-scale observation (a), where the difference in color corresponds to a fluctuation in the thickness of assembled particles. Namely, bright grey-colored region and dark grey-colored region indicate the particles assembled in monolayer (b) and multilayer (c). Assembled region could be extended to 10 mm x 10 mm on large-scale patterned substrate by contact printing, although layer number of particles varied with location of hydrophilic region. Some dark grey-colored regions, assembled particles in multilayer, were also observed on the hydrophobic region (d). The results clearly show the patterned substrate included imperfect structures of OTS layer to be insufficient hydrophobic. The existence of imperfect structures, however, is not experimentally confirmed as described above. These results indicate that the contact angle should be large on hydrophobic region for locational selectivity of particles. Furthermore, the contact angle should be also kept small on hydrophilic region to accurately assemble particles. Namely, it requires optimization of process condition and PDMS mold shape for contact printing to reduce undesirable assembly. Nevertheless, contact printing easily performs scale extension of assembled area, so that it enables self-assembly to become fundamental technique for various devices using self-assembled particles.

5. Conclusion

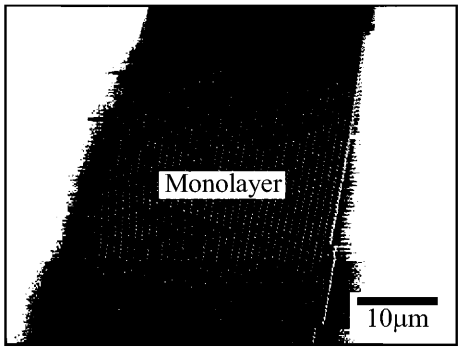
This paper aimed to demonstrate the self-assembly of fine particles by dip coating to hydrophilic/hydrophobic patterned substrates. The results as summarized as follows;

(1) Using electron-beam lithography, self-assembled packed-structure in monolayer can be obtained selectively on the hydrophilic region for water-based suspension.

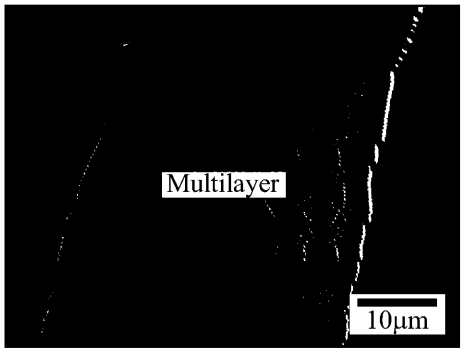
(2) Contact printing process can scale up the size of assembly, 10 mm x 10 mm in this study, though much attention should be paid for printing conditions.



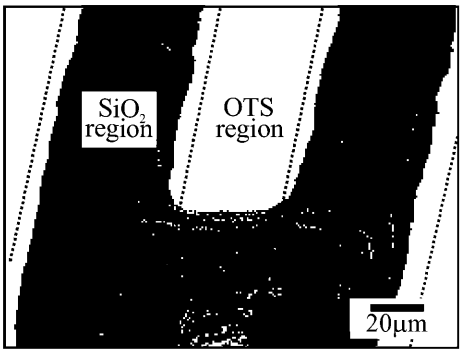
(a) Self-assembled particles on large-scale (10mm x 10mm) area



(b) Monolayer region



(c) Multilayer region



(d) Assemby on OTS region

Fig. 11 Assembled results after 15 times iteration on large-scale patterned substrate fabricated by contact printing method (W_{SiO2} = 50 μm , W_{OTS} = 45μm).

References

(1) Hirai, T., Hayashi, S., Lens functions of polymer microparticle arrays, *Colloids and Surfaces A*, Vol. 153, (1999), pp. 503-513.

(2) Yang, H., Zhu, Y., Glucose biosensor based on nano-SiO2 and "unprotected" Pt nanoclusters, *Biosensors and Bioelectronics*, Vol. 22, (2007), pp. 2989-2993.

(3) Xua, J., Zhang, Y., Lia, G., Zhu, J., An electrochemical biosensor constructed by nanosizedsilver particles doped sol–gel film, *Mater. Science and Engineering C*, Vol. 24, (2004), pp. 833-836.

(4) Nakanishi, T., Hiraoka, T., Fujimoto, A., Saito, S., Asakawa, K., Nano-patterning using an embedded particle monolayer as an etch mask, *Microelectronic Engineering*, Vol. 83, (2006), pp. 1503-1508.

(5) Astratov, V. N., et. al., Photonic band gaps in 3D ordered fcc silica matrices, *Phys. Lett. A*, Vol. 222, (1996), pp. 349-353.

(6) Pan, G., Kesavamoorthy, R., and Asher, S. A., Optically Nonlinear Bragg Diffracting Nanosecond Optical Switches, *Phys. Rev. Lett.*, Vol. 78, (1997), pp. 3860-3863.

(7) Asher, S. A., Weissman, J. M., Tikhonov, A., Coalson, R. D., and Kesavamoorthy, R., Diffraction in crystalline colloidal-array photonic crystals, *Phys. Rev. E*, Vol. 69, (2004), pp. 066619-1-066619-14

(8) Meseguer, F., Colloidal crystals as photonic crystals, *Colloids and Surfaces A*, Vol. 270-271, (2005), pp. 1-7

(9) Cojoc, D., Garbin, V., Ferrari, E., Businaro, L., Romanato, F., Fabrizio, E., Laser trapping and micro-manipulation using optical vortices, *Microelectronic Engineering*, Vol. 78-79, (2005), pp. 125-131.

(10) Schnelle, T., Muller, T., Hagedorn, R., Voigt, A., Fuhr, G., Single micro electrode-dielectro phoretic tweezers for manipulation ofsuspended cells and particles, *Biochimica et Biophysica Acta*, Vol. 1428, (1999), pp. 99-105.

(11) Dimitrov, S. A., and Nagayama, K., Continuous Convective Assembling of Fine Particles into Two-Dimensional Arrays on Solid Surfaces, *Langmuir*, Vol. 12, (1996), pp. 1303-1311.

(12) Matsushita, S. I., Miwa, T., Tryk, D. A., and Fujishima, A., New mesostructured porous TiO2 surface prepared using a two-dimensional array-based template of silica particles, *Langmuir*, Vol. 14, (1998), pp. 6441-6447.

(13) Masuda, Y., Itoh, M., Yonezawa, T., and Koumoto, K., Low-dimensional arrangement of SiO2 particles, *Langmuir*, Vol. 18, (2002), pp. 4155-4159.

(14) Kaneko, A., Moronuki, N. Shibata, T., Kogiso, J., Uchida, K., and Kubo, T., An Application of Dip -coating Technique to Fabrication of Self-assembled Microstructure on Hydrophilic/Hydrophobic-patterned Substrate, *Proc. of euspen*, Vol. 2, (2006), pp. 288-291.

(15) van Delft, F. C. M. J. M., van den Heuvel, F. C., Kuiper, A. E. T., Thune, P. C., and Niemantsverdriet, J.W., Micro-contact printing on oxide surfaces for model catalysts using e-beam written masters in hydrogen silsesquioxana, *Microelectronic Eng.*, Vol. 73-74, (2004), pp. 202-208

(16) Kumar, A., Biebuyck, H. A., and Whiteside, G. M., Patterning Self-Assembled Monolayers: Apprications in Materials science, *Langmuir*, Vol. 10, (1994), pp. 1498-1511

(17) Heule, M., Schonholzer, U. P., Gauckler, L., J., Patterning colloidal suspensions by selective wetting of microcontact-printed surfaces, *Journal of the European Ceramic Society*, Vol. 24, (2004), pp. 2733-2739

(18) John, P., M., S., Craighead, H., G., Microcontact printing and pattern transfer using trichlorosilanes on oxide substrates, *Appl. Phys. Lett.*, Vol. 68, (1995), pp. 1022-1024

(19) Jeon, N., L., Clem, P., Jung, D., Y., Lin, W., Girolami, G., S., Payne, D., A., and Nuzzo, R., G., 1997, Additive Fabrication of Integrated Ferroelectric Thin-Film Capacitors Using Self-Assembled Organic Thin-Film Template, *Adv. Mater.*, Vol. 9, (1997), pp. 891-895

(20) Wang, D., Thomas, S., G., Wang, K., L., Xia, Y., Whiteside, G. M., 1997, Nanometer scale patterning and pattern transfer on amorphous Si, crystalline Si, and SiO2 surfaces using self-assembled monolayers, *Appl. Phys. Lett.*, Vol. 70, (1997), pp. 1593-1595

(21) Payne, D., A., Clem, P., G., Monolayer-Mediated Patterning of Integrated Electroceramics, *Journal of Electroceramics 3*, Vol. 2, (1999), pp. 163-172.