Self-assembly of Particle Wires in 2-D Ordered Array

Yoshitake Masuda,* Minoru Itoh, and Kunihito Koumoto
Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603

(Received July 3, 2003; CL-030593)

We developed a novel self-assembly process to fabricate an orderly array of particle wires constructed from a close-packed structure from colloidal solution without preparation of patterned templates. A substrate was immersed into the solution containing particles perpendicular to the liquid surface and the liquid surface was moved downward by evaporation of solution. Particles formed a mono/multi-particle layer and the particle layer was cut by the periodic drop-off of the solution. This process allowed us to fabricate the orderly array of particle wires and to show the high ability of the self-assembly process for fabrication of nano/micro-structures constructed from nano/micro particles or blocks.

Particles show various interesting properties[1] that are not observed in the bulk form of a material. For instance, photonic crystals can be constructed by monodispersed particles. In order to apply these novel properties for future devices, precise particle arrangement techniques to produce desired particle assemblies must be developed.

2-D patterns with steady repeatability in the particle array were achieved by techniques such as the probe technique,[2] electrophotography method,[3] a micro mold method and gravity,[4] a micro mold and a lateral capillary force,[5] and a patterned Au film and drying process of colloidal solution.[6] In addition, patterns with high arrangement accuracy have been realized by several techniques. Selective immobilization of single particles into predetermined positions with respect to adjacent particles was realized by nanolithography.[7,8] These techniques can be used to precisely arrange nano/micro particles. Kim et al.[9] fabricated micropatterns of the fcc (or hcp) structure from polymer particles (200 nm$f$) using a micro mold. We fabricated a pattern of close-packed particle monolayers and several kinds of particle wires[7] on a patterned self-assembled monolayer (SAM) in the solution containing particles. Miyazaki et al.[10] fabricated photonic crystals such as two-dimensional close-packed structure and fcc (or hcp) structure from latex particles (0.6–2 μmf) by the micro-manipulation technique in a scanning electron microscope. Xia et al.[11] brilliantly fabricated large colloidal crystals with their (100) planes of fcc structure oriented parallel to the substrate, which has a 2-D regular array of square pyramidal pits. Ozin et al.[12] fabricated the patterns of fcc colloidal crystal on a chemical etched silicon substrate by microfluidic colloidal crystal self-assembly. Additionally, (100)-oriented colloidal crystals having fcc structure were formed on a substrate which had an array of square pyramid-shaped etch pits by spin-coating colloidal crystal self-assembly. Colloidal crystals were fabricated rapidly within lithographic patterned silicon grooves by these self-assembly processes under moderate conditions. We recently developed a process for 2-D self-assembly of spherical particles using a liquid mold and its drying process.[13] We fabricated particle wires that have high accuracy of arrangement at room temperature on hydrophilic regions of a patterned SAM. Particles were assembled to have regularity in their array by capillary force in the drying process though this technique requires a substrate which has a patterned SAM.

Here, we developed a novel self-assembly process to fabricate an orderly array of particle wires constructed from a close-packed structure from colloidal solution without preparation of patterned templates.

Octadecyltrichlorosilane (OTS)-SAM was prepared by immersing the Si substrate in an anhydrous toluene solution containing 1% vol OTS for 5 min under an N_2 atmosphere.[14–18] The contact angles of the ethanol solution or water solution measured 10–20° or 96° on the OTS-SAM, respectively, whereas they were saturated (contact angle <5°) on a silicon wafer.[13]

The OTS-SAM was immersed into ethanol solution (80 mL) containing SiO_2 particles (1000 nm$f$, 10 mg). The bottom of the solution was heated at 70 °C and the condenser tube was kept at the top of solution to cool it. The temperature difference between the top and bottom of the solution was controlled so as to stir and move particles by convection. The surface of the solution was moved on the OTS-SAM surface by evaporation of ethanol. Particles began to assemble at the surface of the solution (Figure 1a) and the particle layer was fabricated by the movement of solution surface (Figure 1b). Further evaporation of solution caused separation of the particle layer and solution surface (Figure 1c) because particles were not supplied sufficiently from the solution. The liquid surface was then dropped off and the particle layer was separated from the solution surface (Figure 1d). The next particle layer was formed by the same procedure described above (Figure 1e). Consequently, separated particle wires, i.e., an array of particle wires, were successfully fabricated by our newly developed method (Figures 1f, 2a–2d).

After having been immersed in the solution which evaporates fast, the substrates were observed by a scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.), an optical microscope (BX51WI Microscope, Olympus Optical Co., Ltd.) with a digital camera (DP50, 5.8 megapixels, Olympus Optical Co., Ltd.) and a computer for capturing data, and a digital video camera recorder (DCR-TRV 50, Sony Corporation) with optical magnifying glass.

The width and interval of particle wires were shown to be about 150 and 200 μm, respectively (Figure 2a). Particle wires were constructed from a close-packed particle structure and their upper side showed high feature edge acuity (Figure 2c). Array of particles was finished suddenly as shown on the bottom side of particle wires (Figure 2d). These observations suggested that particle wires were formed from the upper side and cut by drop-off of the solution, and are consistent with the procedure in Figure 1. The mechanism of the assembly process and control of width, interval and thickness of particle wires are further discussed in a separate article.

Particle wires showed iridescent diffraction (Figure 3)

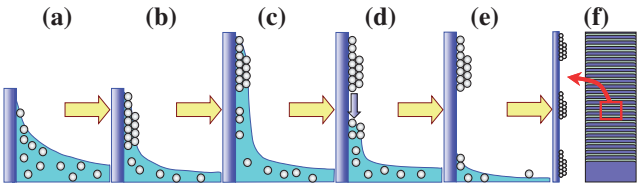

Figure 1. Schematic for self-assembly process to fabricate an orderly array of particle wires constructed from a close-packed structure. (a) beginning of particle arrangement, (b) separation of particle wire and liquid surface, (c) further separation, (d) drop off of solution surface, (e) arrangement of next particle wire, (f) array of particle wires.

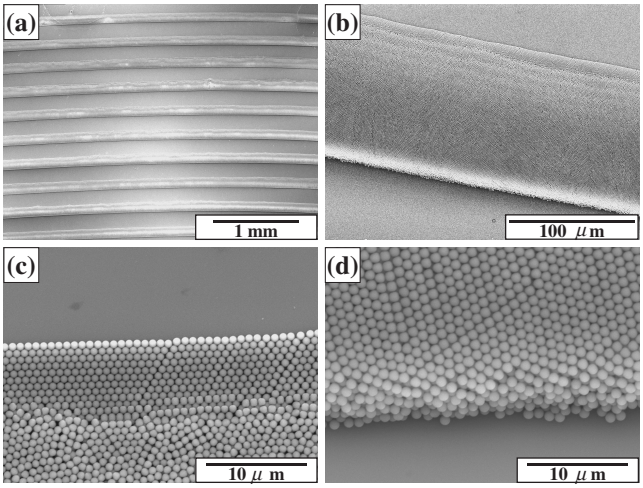

Figure 2. SEM micrographs of array of particle wires. (a) array of particle wires, (b) magnified particle wire, (c) upper side of (b), (d) bottom side of (b).

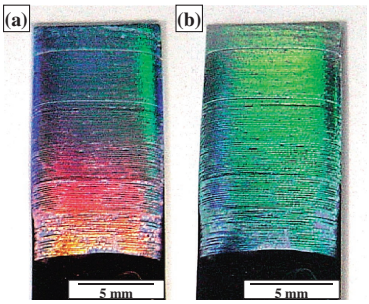

Figure 3. Photographs of particle wires; (a) front shot and (b) cross shot.

caused from the high ordinality of the particle array shown in Figure 2. Diffracted wave number was changed by diffraction angle.

Close-packed structure was easily obtained by the use of capillary force compared to the site-selective deposition in the solution.[7] 2-D ordered array can be fabricated without the preparation of a template though templates are required for liquid mold method.[13]

Additionally, particle wires were formed on the OTS-SAM from the ethanol solution (80 mL) containing a small amount of SiO_2 particles (1000 nm$f$, 1 mg) to fabricate thin wires constructed from a mono-particle layer (Figure 4). Particles were supplied to particle wires slowly from the solution. The number of particle layers was shown to be controlled by the change of particle number in the solution.

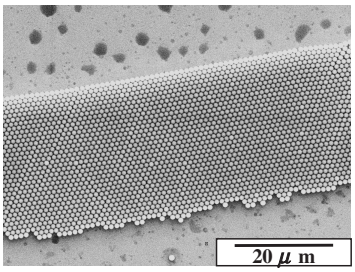

Figure 4. SEM micrograph of a particle wire constructed from a monoparticle layer.

Furthermore, the particle layer was formed on the whole area of OTS-SAM by the use of water which evaporates slowly compared with ethanol. The particle layer was also formed on the whole area of OTS-SAM from ethanol solution sealed in an airtight container which has small holes to evaporate solution slowly. Drop-off of the solution was not observed and particles were supplied to the particle layer continuously. Fast movement of the solution surface caused by quick evaporation or lift of substrate is probably necessary to drop-off the solution surface which allows to fabricate separated particle wires.

Particles were not observed between particle wires formed on hydrophobic OTS-SAM (Figures 2 and 3). OTS-SAM repelled ethanol and extra particles were swept by the drop-off of the solution. On the other hand, many extra particles were observed between particle wires formed on a hydrophilic silicon substrate. Ethanol wetted completely to cover the silicon substrate thinly and leave particles between particle wires in their drying process. Wettability of substrate was shown to be important for removal of extra noise particles.

In summary, we have proposed a novel process to fabricate separated particle wires self-assembly and realized particle wires constructed from a close-packed multi-particle layer or monoparticle layer on OTS-SAM from ethanol solution. The mechanism of this process will be discussed in a separate article, and this process should be improved to fabricate desired nano/micro-patterns of particle assembly.

References

1 Y. Masuda and K. Koumoto, *J. Soc. Inorg. Mater., Jpn.*, **7**, 4 (2000).
2 M. Egashira, T. Konno, and M. Shinya, *J. Intell. Mater. Syst. Struct.*, **7**, 267 (1996).
3 H. Fudouzi, M. Kobayashi, M. Egashira, and N. Shinya, *Adv. Powder Technol.*, **8**, 251 (1997).
4 W. Wen, N. D. W. Zheng, C. Chen, and K. N. Tu, *J. Mater. Res.*, **14**, 1186 (1999).
5 Y. Sun and G. C. Walker, *J. Phys. Chem. B*, **106**, 2217 (2002).
6 Q. Guo, C. Arnoux, and R. E. Palmer, *Langmuir*, **17**, 7150 (2001).
7 Y. Masuda, M. Itoh, T. Yonezawa, and K. Koumoto, *Langmuir*, **18**, 4155 (2002).
8 L. M. Demers and C. A. Mirkin, *Angew. Chem., Int. Ed.*, **40**, 3069 (2001).
9 E. Kim, Y. Xia, and G. M. Whitesides, *Adv. Mater.*, **8**, 245 (1996).
10 H. T. Miyazaki, H. Miyazaki, K. Ohtaka, and T. Sato, *J. Appl. Phys.*, **87**, 7152 (2000).
11 Y. Yin and Y. Xia, *Adv. Mater.*, **14**, 605 (2002).
12 G. A. Ozin and S. M. Yang, *Adv. Func. Mater.*, **11**, 95 (2001).
13 Y. Masuda, K. Tomimoto, and K. Koumoto, *Langmuir*, **19**, 5179 (2003).
14 Y. Masuda, W. S. Seo, and K. Koumoto, *Thin Solid Films*, **382**, 183 (2001).
15 Y. Masuda, W. S. Seo, and K. Koumoto, *Jpn. J. Appl. Phys.*, **39**, 4596 (2000).
16 N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, and K. Koumoto, *Adv. Mater.*, **14**, 418 (2002).
17 N. Shirahata, Y. Masuda, T. Yonezawa, and K. Koumoto, *Langmuir*, **18**, 10379 (2002).
18 Y. Masuda, Y. Jinbo, T. Yonezawa, and K. Koumoto, *Chem. Mater.*, **14**, 1236 (2002).

Published on the web (Advance View) November 5, 2003; DOI 10.1246/cl.2003.1016