Sub-Microstructures Formed by Means of Reactive Ion Etching in Multilayers of Two-Dimensional Fine-Particle Arrays

Sachiko I. Matsushita,[†,††] Yoshie Yagi,[††] and Akira Fujishima*[††]
[†]*Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, 2-1 Hirosawa, Wako, Saitama 351-0198*
[††]*Department of Applied Chemistry, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656*

(Received January 29, 2002; CL-020109)

Highly attractive periodic sub-microstructures were formed in multilayers of two-dimensional fine-particle arrays by means of an oxygen-plasma etching technique. The enhancement of anisotropic etching in multilayers produced these attractive structures, since polystyrene particles (1 μm diameter) in the top layer had worked as protective sidewalls at high power (over 100 W) and low pressure (20 mPa).

Two-dimensional (2D) fine-particle arrays, which can be prepared from monodispersed colloidal particles or protein molecules in a self-assembled system,[1] have attracted much interest from the viewpoints of the orientation of protein molecules, high-density optical memory devices, templates of other structures,[2–4] and photonic crystal slabs,[5–7] because of their attractive features such as short preparation time, large domains, and controllability of the number of the layers in a wide range of particle diameter dimensions (from 19 nm to 40 μm). Moreover, from the viewpoint of the fabrication of submicro- and micro-structures, this self-organization technique needs a relatively simple and inexpensive system compared with other lithography techniques.[8] Nevertheless, conventional 2D arrays produced via self-assembly have an intrinsic disadvantage that precludes widespread applications. Because particles in the suspension are assembled by means of surface tension and capillary forces at the meniscus, permitted morphology is hexagonal high-density packing, which is determined only by the particles' diameter.

Recently, Haginoya, Fujimura, et al. have proposed a simple technique of controlling the morphology of 2D arrays by means of reactive ion etching (RIE).[7,9] They reported an arrayed nanostructure of particles, in which the size of the nanostructure relative to the array pitch can be controlled arbitrarily in monolayers. In this letter, we also report the highly desirable periodic sub-microstructures in multilayers of two-dimensional fine-particle arrays formed by means of RIE.

The details of the preparation of 2D arrays utilizing capillary immersion forces were reported previously.[3] For this self-assembled preparation, the temperature was between 28 and 33 °C and the relative humidity was between 43 and 55%. Under these conditions, the self-assembly speed for preparing mono-layer arrays was 16.0 μm/s. A water suspension of monodisperse polystyrene (PSt) particles ($1.034 \pm 0.020\,\mu$m; Particle-Size Standards, NIST Traceable, Duke Scientific Corp.), 1.0% solids-latex, was used. The substrates were normal glass substrates (Micro-glass slides, Matsunami Co., Japan).

The prepared 2D PSt arrays were etched by an O_2 reactive ion etching apparatus (SAMCO, BP-1) for 30, 60, and 90 s at 50, 100, and 150 W, respectively. The pressure was 20 mPa (this low pressure is said to be desirable for increasing ion bombardment efficiency and achieve anisotropic etching[10]). The structures thus prepared were observed using a scanning electron microscope (SEM) and an atomic force microscope (AFM).

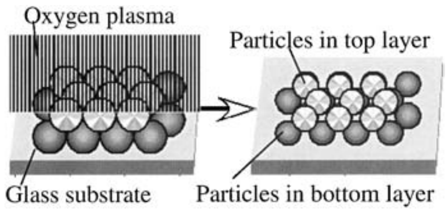

Figure 1. Schematic diagrams showing the preparation procedures for sub-microstructures in multilayers of two-dimensional fine-particle arrays.

From the SEM images of the single layer in 2D PSt arrays (not shown), it was clear that the particle surfaces were etched by O_2 RIE, and the particle diameter became smaller than 1 μm (the original diameter). As easily imagined, the etched particle diameter at 150 W is smaller than that at 50 W. The AFM images also show that the polystyrene particle surfaces were more roughly etched at 150 W than the former ones, especially in the vertical direction. As etching time increased, the particle diameter decreased for each etching power. These results show that the spatially-controllable 2D particle arrays, in which the particle diameter relative to the array pitch can be controlled arbitrarily, were obtained by changing the oxygen RIE power and etching time, as Haginoya et al. had reported partially.[9]

Next, we report the characteristic structures in the double layer of 2D PSt arrays after etching for 30, 60, and 90 s at 100 W (Figure 2). In each image, the glass substrate is shown in black, and the first and second layers from the glass substrates are shown in dark gray and gray, respectively. After etching for 30 s (Figure 2a), it appears that the particle surfaces were etched so that they were round and they kept the spherical shape, which is the same result obtained for a single layer (not shown). However, as the etching time became longer, the PSt particles did not maintain the spherical shapes in the case of double layers. We observe that the gaps, where PSt particles did not exist in either the first or the second layer, were selectively etched in three directions (we can see the glass substrate through this gap as a black triangle in Figure 2b). After 90 s of etching, the particles were more extensively etched through the gaps, and the original spherical shapes were not maintained at all. Instead, highly attractive periodic patterns emerged (Figure 2c). The same phenomena were observed with 150 W etching, but not at 50 W. These results show that at least in the case of more than 100 W at 20 mPa in the multilayer arrays, we cannot use Haginoya et al.'s assumption, which states that the vertical etching rate is approximately the same regardless of surface position.[9]

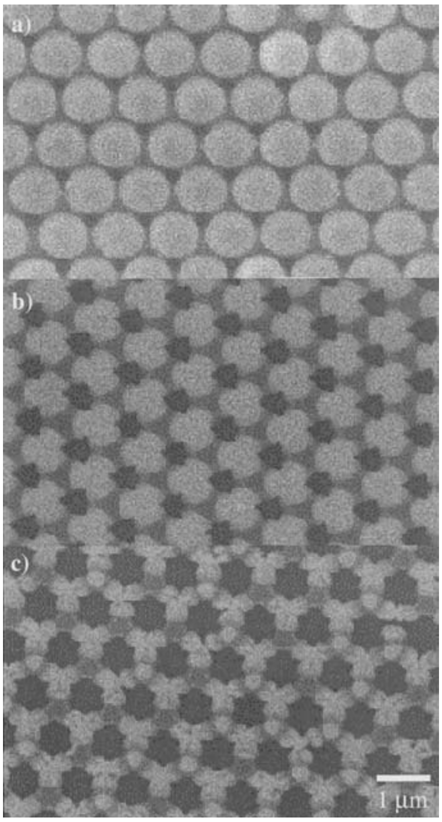

Figure 2. Scanning electron micrographs of double layer of two-dimensional fine-particle arrays after reactive ion etching for (a) 30, (b) 60, and (c) 90 s at 100 W. The diameter of the original latex particle is 1 μm. In each image, the glass substrate is shown as a black part, the bottom layer is shown as a dark-gray part, and the top layer is shown as a gray part.

Now we consider the possibility that chemical species, such as atoms and radicals, act as the etching agent and cause sidewall passivation[10] in the small gaps between the particles. Some researchers have reported that the etching of photoresist may enhance anisotropic etching,[11] i.e., for very reactive materials, plasma etching is conducted at low ion bombardment energies and the formation of vertical blocking layers is essential to prevent undercutting of the mask. Even though this requires further discussion, there is a possibility that the polystyrene walls surrounding the etched gaps might work as protective sidewalls and enhance the anisotropic etching.

We are hopeful that these highly attractive periodic sub-microstructures will expand the wide applications of 2D arrays, especially in the preparation of other periodic structures such as templates or masks.

We thank Dr. A. S. Dimitrov (DBS, NCI, NIH, FCRDC) for development of the glass cell used in the preparation of the particle coating and Dr. Tetsuya Miwa (Japan Marine Science & Technology Center, Japan) for valuable discussions.

References and Notes

1 N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, and K. Nagayama, *Nature*, **361**, 26 (1993).

2 O. D. Velev, T. A. Jede, R. F. Lobo, and A. M. Lenhoff, *Nature*, **389**, 447 (1997).

3 S. Matsushita, T. Miwa, and A. Fujishima, *Langmuir*, **13**, 2582 (1997).

4 S. Okuyama, S. I. Matsushita, and A. Fujishima, *Chem. Lett.*, **2000**, 534.

5 S. I. Matsushita, Y. Yagi, T. Miwa, D. A. Tryk, T. Koda, and A. Fujishima, *Langmuir*, **16**, 636 (2000).

6 R. Shimada, A. Imada, T. Koda, T. Fujimura, K. Edamatsu, T. Itoh, K. Ohtaka, and K. Takeda, *Mol. Cryst. Liq. Cryst.*, **37**, 95 (1999).

7 T. Fujimura, T. Tamura, T. Itoh, C. Haginoya, Y. Komori, and T. Koda, *Appl. Phys. Lett.*, **78**, 1478 (2001).

8 P. Visconti, C. Turco, R. Rinaldi, and R. Cingolani, *Microelectron. Eng.*, **53**, 391 (2000).

9 C. Haginoya, M. Ishibashi, and K. Koike, *Appl. Phys. Lett.*, **71**, 2934 (1997).

10 C. Cardinaud, M.-C. Peignon, and P.-Y. Tessier, *Appl. Surf. Sci.*, **164**, 72 (2000).

11 F. H. Bell, O. Jouvert, and L. Vallier, *J. Vac. Sci. Technol. B*, **14**, 1796 (1996).