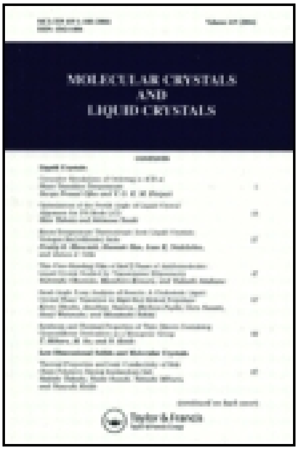

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Control of Structures of Two-dimensional Patterns of Nanoparticles by Dissipative Process

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In this report, we will describe about control of structures of two-dimensional patterns of nanoparticles. When the glass substrate was dipped into and withdrawn from highly concentrated dispersion of nanoparticles, stripe-crack patterns were formed parallel to the receding direction. The patterned assembly of nanoparticles was spontaneously removed from glass substrate. From scanning electron microscopy (SEM), it was clear that the assembly of silica particles had strap-like structure. The thickness of the assembly consisting of silica particles could be controlled by deposition speed and size of particles.

Keywords: crack formation; dissipative structures; nanoparticles; self-organization; two-dimensional patterns

INTRODUCTION

The crack phenomenon is well known and very important problem from Old Stone Age, when our ancestors prepared chipped stone tools [1]. However, theoretical research was begun about 80 years ago [2]. In addition, these researches were mainly performed about cell pattern. Allein *et al.* firstly reported about experimental research and simulation of

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formation of stripe-crack pattern in dried film of colloidal dispersion [3]. Okubo *et al.* and Yang *et al.* also described about crack-stripe pattern in cast film of colloidal particles [4,5]. Until now, the mechanism for formation of "regular" stripe patterns in cast film was not cleared. There have been a few researches for application of the stripe-crack patterns as functional materials.

In this research, we aimed investigation about the formation of "regular" crack-stripe patterns in cast film to prepare functional materials. We have already reported that some types of submicrometer-sized regular patterns were formed in cast films by simple casting of polymer solution or ultra-fine particles dispersion [6–10]. For example, regular stripe patterns were formed parallel to the receding direction of casting solution, when ultra-diluted solution of particles was cast onto freshly cleaved mica surfaces. These patterns were formed by so-called dissipative structures, which were occurred in the edge of droplet on solid substrate. We have tried to prepare the mesoscopic patterns from concentrated colloidal dispersion.

EXPERIMENTAL

Silica particles aqueous dispersion (diameter: 0.03, 0.1, 0.2 μm) was purchased from Nissan Chemical Industries, Ltd. Dispersion of particles were diluted with water purified by Milli-Q SP TOC Reagent Water System (Millipore Corp.). Slide glass (purchased from MATSUNAMI) was dipped into silica dispersion. After about 5 sec, the slide glass was withdrawn from dispersion at constant rate. The films prepared on slide glass were observed by with BHT biological microscope system (OLYMPUS Optical Co. Ltd.). SEM was performed with S-5200 (HITACHI Ltd.).

RESULTS AND DISCUSSION

When droplet of silica particles aqueous dispersion (diameter: 0.1 μm) was cast onto glass substrate, regular stripe patterns were formed parallel to the receding direction after evaporation of solvent (Fig. 1). By SEM, it was suggested that the stripe patterns were caused from cracking of particle's film. With lifting method, the crack patterns were also formed parallel to the lifting direction. After formation of crack patterns, the dried film was spontaneously removed from glass substrate. As a result, self-supported fibrous assemblies of nanoparticles were formed by self-organization (Fig. 2). The length of fibrous assembly was controlled by changing distance of lifting on solid substrate. In addition, regular stripe patterns were left in the whole of

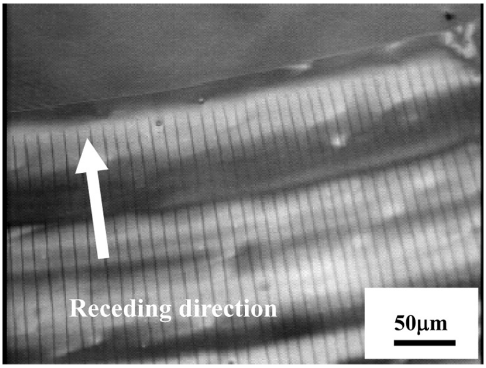

FIGURE 1 Optical micrograph of casting process of silica particles dispersion on glass substrate (diameter of silica particles: 0.03 μm).

slide glass after removal of fibrous assembly of silica particles (Fig. 3). Cross sectional images of self-supported assembly of silica particles by SEM were shown in Figure 4. It was suggested that the assembly had strap-like structure. On the surface of assembly, silica particles were closely packed. The thickness of assembly was getting smaller with increasing the deposition speed. The thickness of assembly was also affected by size of particles. When size of particles was smaller, the

FIGURE 2 Photograph of self-supporting assembly of silica particles on petri dish (diameter of silica particles: 0.1 μm).

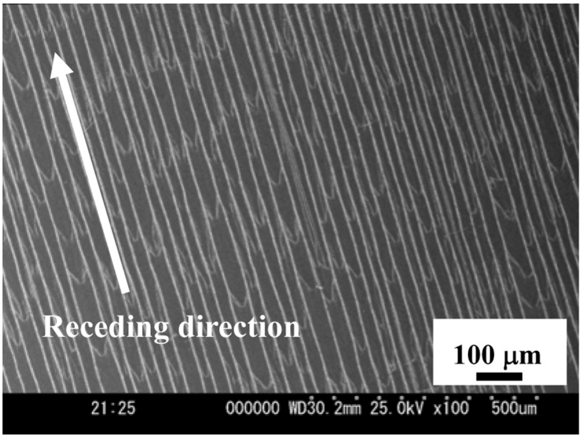

FIGURE 3 SEM image of glass substrate after removal of self-supporting assembly of silica particles (diameter of silica particles: 0.1 μm).

thickness of assembly was getting smaller. Because the crack pattern was formed by shrinking of particle's film, when drying speed was high, number of cracking was increased [5]. Indeed, by increasing deposition speed or decreasing size of particles, the thickness of film

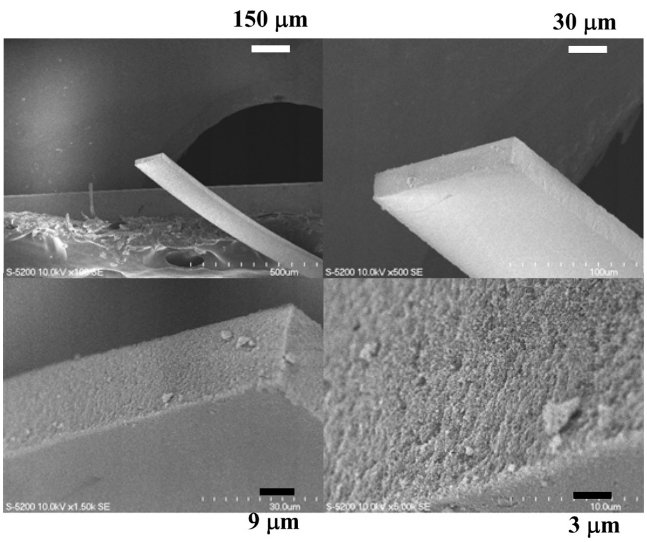

FIGURE 4 SEM image of self-supporting assembly of silica particles (diameter of silica particles: 0.1 μm).

became smaller. The results suggest that control of size of assembly is possible by changing deposition speed or size of particles.

In summary, self-supporting assembly consisting of ultra-fine particles was formed on glass substrate. Strap-like assembly of silica particles spontaneously was removed from glass substrate. Particles were closely packed in the structure. Because the three-dimensional structures were readily formed by self-organization, the process of formation of self-supported assembly is expected to be low-cost preparation method for the photonic devices.

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