Nano/micro patterning of ceramic thin films and fine particles

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We have proposed novel methods for nano/micro patterning of ceramic thin films and fine particles. Self-assembled monolayers (SAMs) were used as templates to realize site-selective deposition (SSD) of thin films or particles. Interaction between SAMs and depositions such as thin films or particles was controlled to fabricate patterns of them.

We have first developed a novel method for SSD of anatase TiO_2 using a seed layer. It was found the nucleation and initial growth of anatase TiO₂ were accelerated on amorphous TiO₂ compared with silanol, amino, phenyl or octadecyl groups. Anatase TiO_2 was selectively deposited on amorphous TiO_2 of a patterned template which has octadecyl groups regions and amorphous TiO₂ regions. Consequently, a micropattern of anatase TiO₂ thin film was successfully fabricated in an aqueous solution.

Furthermore, we developed a novel self-assembly process to fabricate patterns of colloidal crystal. Colloidal solution was dropped onto a patterned SAM having hydrophobic regions and hydrophilic regions to use as a mold for patterning. Particle wires constructed from a close-packed structure or non-close-packed structure, i.e. square lattice, were formed between two droplets and colloid crystals such as an opal structure were formed at both ends of the particle wire after drying the solution.

Key words: patterning, site-selective deposition, self-assembled monolayer, molecular recognition, TiO₂, colloid crystal

1. INTRODUCTION

Nano/micro patterning of thin films or particles has been realized by several methods. We have reported direct site-selective deposition (SSD) of amorphous TiO_2 thin films¹⁻³ or ZrO_2 thin films⁴. A patterned self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS) which has silanol groups and octadecyl groups was used as a template. Amorphous TiO₂ was selectively deposited on silanol regions using the hydrolysis reaction of Ti precursors such as titanium dichloride diethoxide (TDD) from TDD solution¹⁻² or TDD vapor³ and produced micropatterns of TiO₂ that had high feature edge acuity. Saito et al.⁵⁻⁶ fabricated a micropattern of ZnO thin film using a micropattern of catalyst. Pd colloids were selectively adhered to phenyl group regions of a patterned SAM which had silanol groups and phenyl groups. This substrate was then soaked in an aqueous solution of Zn(NO₃)₂ and dimethylamineborane at 55°C for 30 min. The rate of chemical reaction to generate ZnO is increased by Pd colloids which act as a catalyst. ZnO particles of about 0.2 μ m in diameter were thus selectively deposited on Pd colloid regions to fabricate a micropattern of ZnO thin films. A micropattern of HAp fabricated (hydroxyapatite) thin films was bv electrostatic interaction⁷. A patterned SAM of aminopropyltriethoxysilane (APTS) which has amino groups and silanol groups was immersed in an aqueous solution. Negatively charged HAp particles were attracted to positively charged amino groups by static attractive interaction. Particles adhered to the amino groups were further grown to connect with each other and form thin films on regions of amino groups. Moreover, site-selective immersion was realized using a SAM having a pattern of hydrophilic and hydrophobic surfaces⁸⁻⁹. In the experiment the solution containing Ti precursor contacted the hydrophilic surface, and briefly came in contact with the hydrophobic surface. The hydrophilic surface solution was replaced with fresh solution by continuous movement of bubbles, thus anatase TiO₂ was deposited and thin film was grown on the hydrophilic surface selectively. This technique can be used to fabricate any kind of micropattern so long as the film can be deposited from a solution. However, feature edge acuity must be improved if these patterns are to be applied to nano- and micro-sized devices.

Moreover, patterns of particles or colloidal crystals have been reported by several groups. Selective immobilization of single particles into predetermined positions with respect to adjacent particles was realized precise We demonstrated bv nanolithography. arrangement of SiO2 particles (500 nmq) at desired positions by nanolithography using an AFM probe¹⁰ Mirkin et al.¹¹ arranged polystyrene latex particles (190 nmø, 930 nmø, 1 umø) 011 MHA (16-mercaptohexadecanoic acid) dots deposited by holding the AFM probe. These techniques can realize precise arrangement of nano/micro particles. Kim et al. fabricated micropatterns of the fcc (or hcp) structure from polymer particles (200 nm ϕ) using a micro mold. We recently reported a novel process to produce a pattern of close-packed particle monolayers and several kinds of particle wires¹⁰. A SAM of OTS was modified to adopt a pattern of silanol groups and octadecyl groups. The patterned SAMs were then immersed into the solution containing SiO₂ particles. Particles were arranged selectively on regions of silanol groups in the solution, and thus, micropatterns and wires of particles were fabricated. Xia et al.¹³ brilliantly fabricated large colloidal crystals with their (100) planes of fcc structure

oriented parallel to the substrate, which has a two-dimensional regular array of square pyramidal pits. 3D opaline lattices having such orientation over areas as large as several square centimeters were constructed from polystyrene particle (250 nm\u00c6, 480 nm\u00c6, 1.0 \u00c4 m\u00c6) in the solution through self-assembly. This technique does not need special devices such as electron beam writing in the assembling process and the silicon templates should be robust enough to be used many times. Ozin et al.14 described two processes, microfluidic colloid crystal self-assembly and spin-coating colloid crystal self-assembly, for particle assembly on silicon wafers. Patterns of V-shaped grooves inside a Si (100) were prepared by chemical etching to be used as templates for microfluidic assembly. A drop of an aqueous dispersion of SiO₂ particles (840 nm ϕ) was added at the interface between the patterned silicon wafer and the flat block to fabricate the patterns of fcc colloid crystal parallel lines. Additionally, a particle suspension was spread on the wafer having an array of square pyramid-shaped etch pits by spin coating. (100)-oriented colloid crystals having fcc structure were formed in etched pits within 2 h. Colloid crystals were fabricated rapidly within lithographic patterned silicon grooves by these self-assembly processes under moderate conditions.

In this study we developed novel methods to realize SSD of thin films or particles. We first developed SSD of anatase TiO_2 thin films from an aqueous solution using a seed layer. Additionally, we developed liquid mold method to realize site-selective deposition of particles to prepare patterns of colloidal crystal. Interaction between SAMs and depositions such as thin films or particles was controlled to make a pattern of them in these processes.

2. SAM PREPARATION

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 atmosphere¹⁵⁻¹⁹. OM-SAM. PM-SAM and OM-SAM, PM-SAM AET-SAM were prepared by immersing the Au-coated quartz crystal of a quartz crystal microbalance (QCM; QCA917, Seiko EG&G Co., Ltd.) in a dicyclohexyl solution containing 1 vol% octadecylmercaptan (OM), phenylmercaptan (PM) or 2-aminoethanethiol (AET), respectively, for 30 min under an N₂ atmosphere. Substrates with SAMs were then rinsed with anhydrous toluene to remove residual reagents. OM-SAM, PM-SAM and AET-SAM have octadecyl, phenyl or amino groups, respectively. OTS-SAMs were exposed for 2 h to UV light (184.9 nm) through a photomask. The UV-irradiated regions became hydrophilic owing to the formation of Si-OH groups, while the non-irradiated part remained unchanged, i.e., it was composed of hydrophobic octadecyl groups, which gave rise to patterned OTS-SAM. This patterned SAM was used as a template for SSD of amorphous TiO₂ thin films¹⁻² or liquid mold method. SAMs on quartz crystals of a QCM were exposed for 2 h to UV light without a photomask to assess the deposition rate of anatase TiO₂ on hydroxyl groups (OH) instead of on silanol groups (Si-OH). To check the successful formation of films and change of functional group, water drop contact angles were measured for irradiated and non-irradiated surfaces. Initially deposited OTS-SAM, OM-SAM, PM-SAM and AET-SAM showed water contact angles of 96°, 96°, 76° and 53°, respectively. UV-irradiated surfaces of SAMs (OH-SAM) were, however, wetted completely (contact angle $< 5^\circ$).

3. PATTERNING OF ANATASE TiO_2 THIN FILMS USING A SEED LAYER

3.1 Quantitative analysis of the deposition of anatase TiO_2 onto an amorphous TiO_2 thin film or onto SAMs.

Quartz crystals covered with amorphous TiO₂ thin film, OM-SAM (CH₃), PM-SAM (Ph), AET-SAM (NH₂) or OH-SAM (OH) were immersed in a solution¹⁵ containing 0.05 M TiF₆²⁻ and 0.015 M BO₃³⁻ at pH 1.5 or pH 2.8 (Fig. 1). The supersaturation degree of the solution at pH 1.5 was low as the high concentration of H^+ suppressed TiO_2 generation, and hence the deposition reaction progresses slowly with no homogeneous nucleation occurring in the solution. We found that anatase TiO₂ was deposited on an amorphous TiO₂ thin film faster than on OM-, PM- AET- or OH-SAMs at pH 1.5. This shows that the deposition of anatase TiO₂ was accelerated on amorphous TiO₂ compared with on silanol, amino, phenyl or octadecyl groups. TiO₂ probably decreases Amorphous the nucleation energy of anatase TiO₂. The difference in deposition rate enables SSD to be achieved. The amorphous TiO₂ thin film can be used as a seed layer to accelerate the deposition of anatase TiO₂. The deposition rate at pH 2.8 was larger than that at pH 1.5 because of the high degree of supersaturation, and homogeneously nucleated particles in the solution deposited on the whole surface of the substrate, regardless of the surface functional groups. The thickness of anatase TiO₂ thin film deposited on a quartz crystal covered with amorphous TiO₂ at pH 1.5 for 1 h and at pH 2.8 for 30 min was estimated to be 36 nm and 76 nm, respectively, assuming the density of anatase type TiO_2 to be 3.89 g/cm³.



Fig. 1. Deposition quantity of anatase TiO_2 on amorphous TiO_2 , octadecyl groups, phenyl groups, amino groups or hydroxyl groups at pH 1.5 or pH 2.8 as a function of deposition time.

3.2 SSD of anatase TiO2 using a seed layer

A micropattern¹ having amorphous TiO₂ and octadecyl groups was immersed in an aqueous solution¹⁵ at pH 1.5 for 1 h (Fig. 2). Deposited thin films made it appear white compared with octadecyl group regions in SEM micrographs (Fig. 3 (2-a), (2-b)) because of the difference in height. The feature edge acuity of antase TiO₂ pattern was ~ 2.1 % variation (i.e., 0.5 / 23.2) and was much the same as we calculated from amorphous TiO₂ pattern. This resemblance was observed from Fig 3 (1-a) and (2-a). These micrographs were taken from the same position. Variations of these patterns were much better than that of the pattern fabricated with a lift-off process and the usual 5 % variation afforded by current electronics design rules. Additionally, these variations were similar to that of a TEM mesh (2.1 %) we used as a photomask for Fig. 3. Therefore, variations of these patterns can be improved through the use of a high resolution photomask. The thin films were evaluated by an X-ray diffractometer (XRD; RAD-C, Rigaku) with CuKa radiation (40 kV, 30 mA) and Ni filter plus a graphite monochromater. Deposited films showed weak XRD patterns of anatase type TiO₂ because the films were not sufficiently thick to show strong diffraction. This finding provides evidence for the deposition of anatase TiO₂ on amorphous TiO₂ regions. An atomic force microscope (AFM; Nanoscope E, Digital Instruments) image showed anatase TiO2 thin films to be higher than octadecyl group regions (Fig. 4). The center of the anatase TiO₂ thin film region was 61 nm higher than the octadecyl regions, and the thickness of the anatase TiO₂ thin film was estimated to be 36 nm considering the thickness of amorphous TiO2 thin film (27 nm)¹⁻² and OTS molecules (2.4 nm) (Fig. 2).



Fig. 2. Conceptual process for site-selective deposition of anatse TiO_2 thin films using a seed layer.

This result is similar to that estimated by QCM measurement (36 nm). The surface roughness (RMS) of the anatase TiO₂ thin film was estimated using an AFM image. The AFM image showed the film roughness to be 3.7 nm (horizontal distance between measurement points: 6.0 μ m) (Fig. 4-(a)), which is less than that of amorphous TiO₂ thin film (RMS 9.7 nm, 27 nm thick, horizontal distance between measurement points: 6.0 μ m))¹⁻². Additionally, the roughness of the octadecyl group regions was shown to be 0.63 nm (horizontal distance between measurement points: 1.8 μ m) (Fig. 4-(b)).



Fig. 3. SEM micrographs of (1-a), (1-b) a micropattern of amorphous TiO₂ thin films and (2-a), (2-b) a micropattern of anatase TiO₂ thin films deposited at pH=1.5.



Fig. 4. AFM image, cross section profile and (a), (b) measurement areas of surface roughness of a micropattern of anatase TiO_2 thin films deposited at pH 1.5.

Amorphous TiO₂ accelerated the deposition of anatase TiO₂ and showed its excellent performance as a seed layer. The feature edge acuity of anatase TiO2 patterns was estimated to be approximately 2.1% using the same method as used for a micropattern fabricated by the lift-off process and was the same as that of amorphous TiO_2^1 . The feature edge acuity could be improved by using a higher feature edge acuity photomask since this variance is similar to that of the TEM mesh (2.1%). XRD measurements for the thin film deposited for 1 h did not show any peaks since the deposited quantity was not sufficient to show any diffraction, however, the thin film deposited for 7 h was composed of anatase TiO₂. Anatase TiO₂ thin films were not peeled off by sonication in ethanol for 10 min and showed strong adhesion to the amorphous TiO₂ layer. This suggests that strong chemical bonds were formed between anatase TiO2 and amorphous TiO2.

4. PATTERNING OF PARTICLES USING LIQUID MOLD METHOD

4.1 The dispersibility of particles in the solution

The dispersibility of particles in the solution is very important for particle assembly and high dispersibility is necessary to form a close-packed structure. The zeta potentials of particles dispersed in the solutions were examined by direct measurement of electrophoretic mobility using an electrophoretic light scattering spectrometer (Zetasizer 3000HS, Malvern Instruments Co., Ltd.). The zeta potentials of polystyrene particles (550 $nm\phi$) in water, carboxylated particles (820 $nm\phi$) in water, polystyrene particles in ethanol and carboxylated particles in ethanol were determined to be -38.3mV, -50.2mV, -53.9mV and -44.0mV, respectively. Surface modification by carboxyl groups decreased the negative zeta potential in both solutions. Furthermore, particles in the ethanol had slightly low negative zeta potentials compared to those in water, i.e. the particles were slightly well-dispersed compared to those in water.

4.2 Patterning of particles by liquid mold method

An SAM of OTS was formed on a silicon substrate and modified by UV irradiation to create a pattern of hydrophobic octadecyl and hydrophilic silanol groups. Ethanol or water containing particles (550 nm φ or 800 nm φ) was dropped onto a patterned SAM (Fig. 5). The solution was separated into two droplets with a liquid bridge between the droplets along the hydrophilic regions of a patterned SAM. The droplets and the liquid bridge were used as a mold for fabrication of a two-dimensional pattern of colloid crystals. Particle wire was formed between two droplets and colloid crystals such as an opal structure were formed at both ends of the particle wire after drying the solution.

The water at the liquid bridge evaporated in about 24 h to form a particle wire, and droplets at the two ends completely evaporated in about 48 h. In this manner, particle wires constructed from a



Fig. 5. Conceptual process for fabrication of a particle wire using a patterned SAM and a liquid bridge.

close-packed structure, i.e. triangular lattice, were produced from the water solution (Fig. 6a). The middle of a particle wire was narrower than its end (Fig. 6c). The width of the particle wire does not depend on the width of the silanol line, but rather on the interfacial tensions between solution and substrate, solution and atmosphere, and atmosphere and substrate. The silanol line was not used to decide the width of the particle wire, but rather the position of the liquid bridge and particle wire. Close-packed structures were also formed on large silanol regions (Fig. 6d, e, f). The right-hand area of Fig. 6e can be regarded as the {100} plane of the fcc structure and the left-hand area can be regarded as the {111} plane of the fcc structure or the {0001} plane of the hcp structure. The close-packed structure was thus considered to be an fcc structure.



Fig. 6. SEM micrographs of particle structures fabricated from aqueous solution containing micro particles using a liquid bridge. (a)-(c) particle wires and (d)-(f) a close-packed 3D structure.

Figure 7 shows particle wires and 3D structures fabricated from ethanol solution containing polystyrene particles. The ethanol at the liquid bridge evaporated in about 1 min to form a particle wire, and droplets at the two ends evaporated in about 20 min. The liquid bridge of ethanol evaporated faster than that of water for several reasons. The saturated vapor pressure of ethanol (59 mmHg (0.078 atm) at 25°C) is higher than that of water (24 mmHg (0.031 atm) at 25°C), explaining the difference in the evaporation rate of the two droplets. The ratio in evaporation rate of the ethanol liquid bridge to the ethanol droplets is higher than that of the water liquid bridge to the water droplets. This can be explained as follows: Water has high surface tension (71.8×10⁻³ N/m at 25°C) compared with ethanol (22.0×10⁻³ N/m at 25°C). Ethanol existed along patterned hydrophilic regions with small meniscus at the angle between droplets and a liquid bridge. However, water formed large meniscus at the angle between droplets and a liquid bridge, causing a wide line width of water liquid bridge compared with ethanol on our patterned surfaces. Additionally, the water liquid bridge was higher than that of ethanol due to high surface tension. These made the cross-section area of water larger than that of ethanol. The thick liquid bridge evaporated slowly because of its large volume and low vapor pressure calculated from the Kelvin equation in which the smaller convex liquid surface gives rise to higher internal pressure and faster evaporation rate²⁰ Furthermore, the solution at the droplets flowed into a liquid bridge and this further complicated the evaporation mechanism.



Fig. 7. SEM micrographs of particle structures fabricated from ethanol solution containing micro particles using a liquid bridge. (a), (b) particle wires constructed from square lattice and (c), (d) close-packed 3D structures.

A narrow particle wire was formed at the center of the liquid bridge (Fig. 7a, b), and wide wires were formed at the edges of the liquid bridge along the silanol line. The particle wire in Fig. 7a is not a close-packed structure and is

constructed from a square lattice, which is a metastable phase compared with a close-packed structure. High dispersibility of particles is necessary to form a close-packed structure in the solution. However, the particles dispersed well in ethanol and the dispersibility of particles in ethanol is similar to that in water. This shows that the non-close-packed structure was caused not only by the influence of dispersibility but also by many other factors. Movement and rearrangement of deposited particles is necessary to construct a close-packed structure. However, the ethanol evaporated quickly and suppressed the movement of particles by liquid bridge force. Additionally, adhesion between particles and a substrate, and cohesion between particles probably caused moderate suppression of the rearrangement of particles. Factors such as evaporation rate, interaction force between particles, and interaction force between particles and a substrate were important in the packing process. Close-packed 3D structures were also formed on large silanol regions (Fig. 7c, d), and they contained many defects (Fig. 7d). The ethanol evaporated so quickly that the particles did not rearrange well to form a close-packed structure during evaporation of ethanol. This is one of the factors of forming a loosely packed structure. To directly evaluate the effect of the evaporation rate, a similar experiment using ethanol was conducted in a small airtight container with small pinholes to allow the ethanol to evaporate slowly. The size and number of pin holes were adjusted for ethanol at the liquid bridge to evaporate in about 24 h. The particle wire constructed from a close-packed structure was formed after about 24 h, and droplets at both ends were dried after about 48 h. The close-packed 3D structures were formed in large silanol regions. The number of defects was smaller than that formed from the ethanol solution with a shorter time and was similar to that formed from water. The humidity in the container was close to 100% and the saturated vapor pressure of ethanol was 59 mmHg (0.078 atm) at 25°C. This showed that particles dispersed well in ethanol and the interaction between particles and a substrate was sufficiently weak to produce a close-packed structure in the drying process of 24 h. Additionally, the results showed that not only the interaction force between particles and that between particles and a substrate, but also the evaporation rate needs to be controlled to fabricate particle wires.

Accuracy of particle arrangement was evaluated from Fig. 7(a) as calculated in recent work¹⁰. The center position $((x_i, y_i) \mu m)$ of each particle in an upper layer was plotted to estimate the standard deviation. The bottom left corner of Fig. 7(a) was set to be the origin of the x-y coordinate.

The approximated straight line (f(x)) and its slope (θ) are represented as follows.

$$f(x) = 1.3965x - 5.3344,$$
(1)

$$\cos\theta = 0.5822,$$
(2)

Standard deviation from the approximated straight line is described by the expression, S (standard deviation) =

$$\frac{\left[\sum_{i} \left\{\cos \theta \cdot \left(f(x_{i}) - y_{i}\right)\right\}^{2}\right]^{\frac{1}{2}}}{n-1}, \quad (3)$$
where n is the number of particles $(n = 19)$. Th

where *n* is the number of particles (n = 19). The accuracy of the particle arrangement in Fig. 7(a) was estimated to be $S = 1.63 \times 10^{-3}$. This is lower than that of the particle arrangement obtained in our previous work¹⁰.

5. Conclusions

We have developed a novel method to realize SSD of thin films using a seed layer. The deposition of anatase TiO_2 from an aqueous solution was shown by QCM analysis to be accelerated on amorphous TiO_2 thin films compared with on octadecyl, phenyl, amino or hydroxyl groups. A micropattern having amorphous TiO_2 regions and octadecyl regions to be used as a template was prepared and immersed in the aqueous solution. Anatase TiO_2 was successfully deposited on amorphous TiO_2 regions, and amorphous TiO_2 thin film was shown to act effectively as a seed layer to accelerate the nucleation and initial growth of anatase TiO_2 . Consequently, SSD was achieved and a micropattern of anatase TiO_2 was fabricated in the aqueous solution using a seed layer.

Furthermore, we developed a self-assembly process to fabricate particle wires on hydrophilic regions of a patterned SAM. Ethanol or water containing particles was separated into two droplets with a liquid bridge between the droplets along hydrophilic regions of a patterned SAM. Particle wires constructed from a close-packed structure or non-close-packed structure were then formed through self-assembly between two droplets after drying of the solution. Colloidal solution was utilized as a mold to fabricate patterns of colloid crystal.

Molecular recognition between SAMs and depositions such as thin films or particles was utilized for site-selective deposition of them. Patterns of thin films or particles were thus fabricated by our newly developed solution processes.

6. References

[1] Y Masuda, T. Sugiyama, H. Lin, W. S. Seo, K. Koumoto, *Thin Solid Films*, 382, 153-157 (2001).

[2] Y. Masuda, Y. Jinbo, T. Yonezawa, K. Koumoto, *Chem. Mater.*, 14(3), 1236-1241 (2002).

[3] Y. Masuda, W. S. Seo, K. Koumoto, *Langmuir*, 17(16), 4876-4880 (2001).

[4] Y. F. Gao, Y. Masuda, T. Yonezawa, K. Koumoto, J. Ceram. Soc. Jpn., 110(5), 379-385 (2002).

[5] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, K. Koumoto, *Adv. Mater.*, 14(6), 418-421 (2002).

[6] N. Saito, H. Haneda, D. Li, K. Koumoto, J. Ceram. Soc. Jpn., 110(5), 386-390 (2002).

[7] P. X. Zhu, Y. Masuda, K. Koumoto, J. Colloid Interface Sci., 243(1), 31-36 (2001).

[8] Y. Masuda, T. Sugiyama, K. Koumoto, J. Mater.

Chem., 12(9), 2643-2647 (2002).

[9] Y. Masuda and K. Koumoto, "Site-selective Immersion Method", Japanese Patent Application Serial Number 2002-137641, May. 13, 2002.

[10] Y. Masuda, M. Itoh, T. Yonezawa, K. Koumoto, *Langmuir*, 18(10), 4155–4159 (2002).

[11] L. M. Demers, C.A. Mirkin, Angew. Chem. Int. Ed., 40(16), 3069-3071 (2001).

[12] E. Kim, Y. Xia, G. M. Whitesides, Adv. Mater., 8, 245 (1996).

[13] Y. Yin, Y. Xia, Adv. Mater., 14(8), 605-608 (2002).

[14] G. A. Ozin, S. M. Yang, Adv. Func. Mater., 11(2), 95-104 (2001).

[15] Y. Masuda, T. Sugiyama, W. S. Seo, K. Koumoto Chem. Mater., 15(12) 2469-2476 (2003).

[16] Y. Masuda, W. S. Seo, K. Koumoto, *Thin Solid Films*, 382, 183-189 (2001).

[17] Y. Masuda, W. S. Seo, K. Koumoto, Jpn. J. Appl. Phys., 39, 4596-4600 (2000).

[18] Y. Masuda, T. Koumura, T. Okawa, and K. Koumoto, J. Colloid Interface. Sci., 263, 190-195 (2003)
[19] N. Shirahata, Y. Masuda, T. Yonezawa, and Koumoto Langmuir, 18(26), 10379-10385, (2002).

[20] P. W. Atkins, Physical chemistry, Oxford University Press, Oxford (1998).

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