Mesoporous Silica Films Deposited on Micropatterned Organosilane Monolayers

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Based on organized surfactant templating, mesoporous silica films were prepared on molecularly defined and micropatterned surfaces. The substrates were first prepared by forming an organosilane self-assembled monolayer (SAM) on Si wafers employing octadecyltrimethoxysilane as a SAM precursor. A photomask pattern was printed on a SAM surface by vacuum ultraviolet irradiation through the photochemical degradation of the SAM in the irradiated area. These irradiated and unirradiated regions were hydrophilic and hydrophobic, respectively. The mesoporous silica was synthesized in a solution of tetraethylorthosilicate, cetyltrimethylammonium chloride, hydrochloric acid and water. The morphologies of the deposited mesoporous silica on the surfaces of the hydrophilic and hydrophobic regions were found to be quite different, showing the difference in the supramolecular template structures formed on each surface. The spatial control of surfactant-assembling was accomplished.

Key words; mesoporous silica, organosilane self-assembled monolayer, photolithography

1. Introduction

Surfactants have been shown to organize oxide materials into a variety of mesoporous forms, through the mediation of various intermolecular interactions including electrostatic, hydrogen bonding, and hydrophobic interactions.[1-9] Such mesoporous oxides are attracting attention due to its various applications, e.g., filtering, selective catalysis and sensors. When such a mesoporous oxide film grows at a solid/liquid interface, its structure is sensitive to chemical and physical properties of the solid surface since the structure of the mesoporous oxide is governed by the supramolecular structure of the organized surfactant molecules.

Here we report on deposition of mesoporous silica (MPS) films on two types of substrates with hydrophilic or hydrophobic surface. The hydrophobic surface is prepared by forming an organosilane self-assembled monolayer (SAM) on Si wafers. These MPS structures are studied by X-ray diffraction (XRD) and infrared (IR) spectroscopy. The morphologies of the deposited MPS on the hydroxyl and alkyl-terminated surfaces are observed using optical microscope and atomic force microscope (AFM). The difference in the morphologies and structures of the MPS films on these surfaces is discussed in terms of the supramolecular template structures formed on each surface. Furthermore, in order to study microstructure effects on MPS growth, micropatterned SAM substrates are fabricated through photolithography.

2. Experimental

Three types of substrates with hydrophilic, hydrophobic and micropatterned hydrophilic/hydrophobic surfaces were used in this study.

The hydrophilic-surface substrate was prepared through the following procedure. A Si substrate was cleaned through ultraviolet light-generated ozone cleaning. By this cleaning, organic contamination on the substrate was removed and a clean surface oxide was photochemically prepared. This oxide surface was hydroxylated and, therefore, completely hydrophilic with its water contact angle of less than 5°.

The hydrophobic surface substrate was prepared through covering a photo-cleaned Si substrate with an organosilane SAM consisting of octadecylsilyl [$CH_3(CH_2)_{17}Si\equiv$, ODS] groups. The SAM was prepared by chemical vapor deposition (CVD) using n-octadecyltrimethoxysilane as a precursor. Its thickness of the monolayer was estimated by ellipsometry to be 1.8 ± 0.2 nm. The monolayer surface was hydrophobic showing a water contact angle of ca. 105°. The details of this CVD method have been published elsewhere.[10]

The micropatterned substrate was fabricated by vacuum ultraviolet (VUV) photolithography as schematically illustrated in Fig. 1.[11] A Si substrate coated with the ODS-SAM was irradiated for 10 min with VUV light (an excimer lamp, UER20-172V, Ushio Electric, λ = 172 nm) through a photomask contacting the ODS-SAM surface. Since VUV light of this

wavelength is greatly absorbed by oxygen in air, the substrate and photomask were placed in vacuum (~ 10 Pa) in order to attain sufficient VUV light intensity at the ODS-SAM surface. VUV light dissociatively excites C-C and C-H bonds resulting in the decomposition of organic molecules.[12] Therefore, the ODS-SAM is decomposed and removed in the photoirradiated area. The photoirradiated area of the ODS-SAM became hydrophilic while the unirradiated area remained hydrophobic. The water contact angle of the ODS-SAM changed from 105° to less than 5° after a 10 min irradiation. Consequently, the pattern on the photomask was transferred onto the ODS-SAM as a hydro-philic/-phobic pattern. An AFM image of the photopatterned ODS-SAM is shown in Fig. 1c. The photoirradiated area of 5 μm in width clearly receded from the surrounding unirradiated area. From the cross section of this image, the depth was estimated to be 1.7 ± 0.3 nm which is the almost same as the ODS-SAM thickness. The ODS-SAM seems to have been removed by the photoirradiation. The patterning resolution of the present method was 1 μm or less.

On these three samples, MPS was synthesized. First, cetyltrimethylammonium chloride (CTA, cationic

Fig. 1. SAM micropatterning by VUV photolithography. a), b) Contact printing of a photomask pattern. c) AFM image of a photopatterned ODS-SAM.

surfactant), hydrochloric acid (HCl), and water (H_2O) were mixed and stirred. After CTA powder was completely dissolved, tetraethylorthosilicate (TEOS, silica source reagent) was added to the solution and mixed with stirring for a few minutes at room temperature. The final reactant mole ratios [TEOS : CTA : HCl : H_2O = 0.1 : 0.11 : 7 : 100] were employed. The samples were then immersed in this solution so that their right sides were down. The solution and substrates were kept quiescently for several hours. In such a solution, MPS is considered to be synthesized through the following mechanism. Hexagonal arrays of cylindrical micelles form with the cationic groups of CTA molecules to the outside. Silanol anions produced by hydrolysis of TEOS attracted to the positively charged micelle surface and then occupy the spaces between the micelle cylinders. Consequently, silica is organized to be a mesoporous structure of hexagonal symmetry.

The deposited films were studied by IR absorption spectroscopy (Biorad Laboratories, FTS-175C), XRD (using CuKα radiation with λ = 0.154187 nm, Rigaku Denki, RINT2200), optical microscopy (Nikon, Optiphoto) and AFM (Park Scientific Instruments, Autoprobe-LS). Image SXM[13] was used for proccessing AFM data.

3. Results and discussion

IR spectra of the deposited films on the hydrophilic substrate (MPS/Si) and on the hydrophobic substrate (MPS/ODS) are shown in Fig. 2 as well as that of a naked Si substrate. These films were prepared through 5-hour treatment. The spectra shapes of the MPS films were almost same each other. In the spectra of the both films, there are absorption peaks around 2957, 2922 and 2853 cm^{-1} which do not exist in the spectra of the Si substrate. These peaks are denoted to C-H bonds of the alkane chain of CTA. In addition, IR spectra of deposited films in the region of 1000 ~ 1200 cm^{-1} show adsorption bands corresponding to Si-O-Si bonds. However, these adsorption bands are broader than that of the Si substrate and can be separated into several peaks. This indicates that the deposited films partially contain Si-O-C bonds and, thus, insufficiently hydrolyzed TEOS. Thus, deposited films found to be a composite of CTA and polymerized organosilicate. By calcination, CTA in the films could be removed and the polymerized organosilicate converted to a purer silica form. When the films were calcinated at 300 °C, the adsorption peaks due to C-H disappeared. The adsorption bands in 1000 ~ 1200 cm^{-1} were sharpened as similar to that of the Si substrate and, furthermore, became greater.

Figure 3 shows XRD patterns of the deposited films. Each film shows a diffraction peak centered at $2\theta \cong 2.5°$
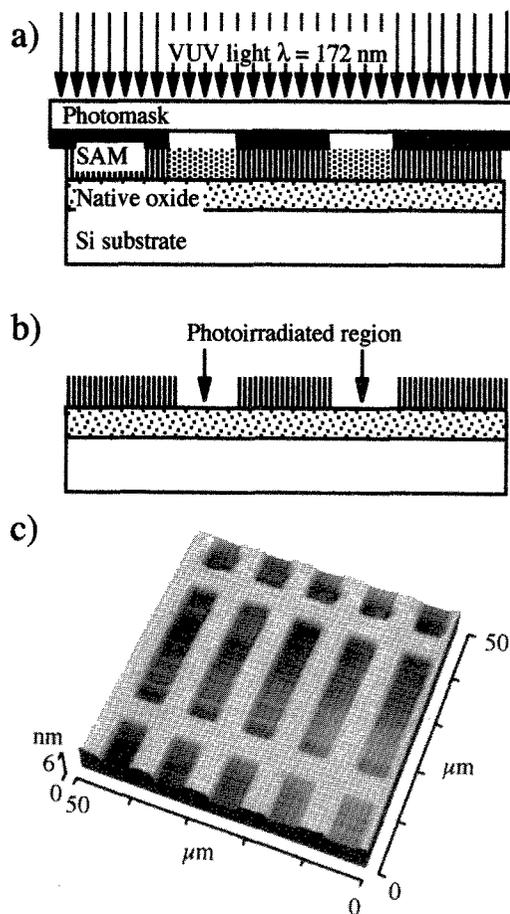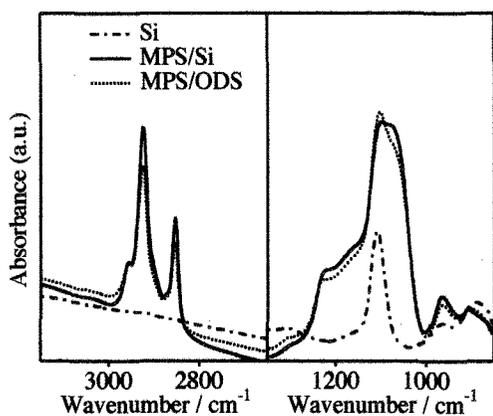
Fig. 2. IR spectra of MPS-depsoited samples.
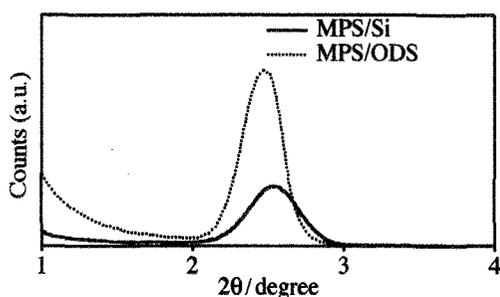
Fig. 3 X-ray diffraction pattern of MPS films.
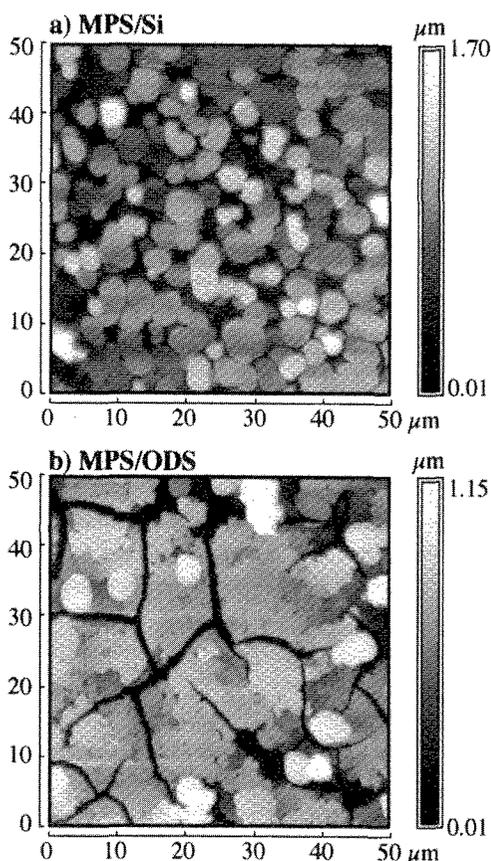
Fig. 4 AFM images of MPS a) on the hydrophilic substrate and b) hydrophobic substrate.

Each film shows a diffraction peak centered at $2\theta \cong 2.5°$ indicating a periodicity of ca. 3.5 nm. The films were proved to have the well documented hexagonal MPS structure.[1,2]

Surface morphologies of the MPS films were observed by AFM. As shown in Fig. 4a, the MPS/Si consists of disk-like structures of 2 ~ 5 μm in diameter and 0.5 ~ 1.0 μm in thickness. Such disk-like structures are typically seen in MPS grown in the same acidic solution.[5] The film growth did not proceed uniformly but seemed to occur certain nucleation sites. The substrate Si surface was exposed between the disks. On the other hand, the MPS/ODS has many cracks which are considered to be formed due to volume shrinkage during dry. Between the cracks, the film surface is relatively flat although a small number of disk-like deposits, similar to those seen in Fig. 4a, exist in the film. The film thickness of ca. 0.7 μm was estimated from the crack depth.

The morphological difference of the MPS films as shown in Fig. 4 must be originated in supramolecular template structures of organized surfactant molecules formed on the substrate surfaces. With hydrophobic surfaces, the surfactant molecules interact primarily through hydrophobic and van der Waals interactions. Accordingly, single-chain quaternary ammonium surfactants, such as CTA, form half-cylindrical aggregates at the bottom of which the surfactant tailgroups and alkane chains are parallel to the substrate as schematically illustrated in Fig. 5.[14] On these surfactant aggregates at the solid/liquid interface, cylindrical micelle rods are thought to be further assembled so as to be aligned to the surface half-micelle array. The channels of the MPS/ODS ran substantially pararell to the substrate. It was also reported that MPS grown on a hydrophobic alkanethiol SAM surface was oriented to be parallel to the SAM surface.[9]

On the other hand, the hydrophobic and van der Waals interactions are not dominant between the Si substrate and CTA. The surface of this hydrophilic Si
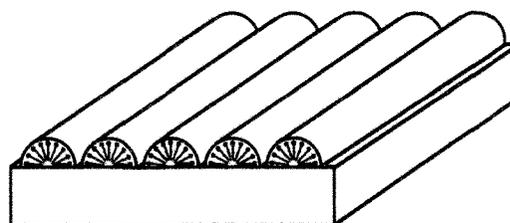
Fig.5 A half-cylindrical micellar array formed on a hydrophobic substrate

substrate is covered with silica of which isoelectric point is about pH = 2.0.[15] Under the present MPS growth condition in which pH value was less than 1, the silica surface would be charged positively. Such a positively charged surface repels cationic surfactant molecules,

e.g., CTA, through the electrostatic interaction. Indeed, it has been reported that the amount of cationic surfactant molecules on silica decreased with an decrease in pH of the surfactant solution.[16] Therefore, the surfactant aggregates as shown in Fig. 5 did not form on the hydrophilic Si substrate.

The disk-like structures existed in the both MPS/Si and MPS/ODS independently of the substrate surface properties, although those on the MPS/ODS were less frequently appeared (Fig. 4a and b). Liquid phase reactions are, thus, primarily responsible to the formation of disk-like structure. The origin of disk-like structure of MPSs is possibly explained by the following argument. First, a small cluster formed from a surfactant assembly and silanol ions in the liquid phase. Since this cluster is less charged than the CTA micelle, the cluster is easier to absorb even on the positively charged surface. The cluster may fix onto a certain position on the surface and serve as a nucleation site. In the case of the MPS/ODS, most of surfactant molecules near the substrate surface were consumed for forming the molecular assemblies as shown in Fig. 5 and, accordingly, the number of the cluster became smaller.

In final, experimental results on the MPS growth on micropatterned substrates are shown. An example is shown in Fig. 6. This is an optical micrograph captured in a dark-field mode which images scattered light at the sample surface. By this observation, a rougher surface is imaged brighter. The bright region in the picture corresponds to the MPS film deposited on the photoirradiated area, where hydrophilic, while the dark region corresponds to the MPS film on the unirradiated ODS surface. As confirmed by AFM, the MPS on the photoirradiated hydrophilic area was rough as similarly shown in Fig. 4a, while the MPS on the unirradiated hydrophobic ODS surface was relatively smooth as similarly shown in Fig. 4b.
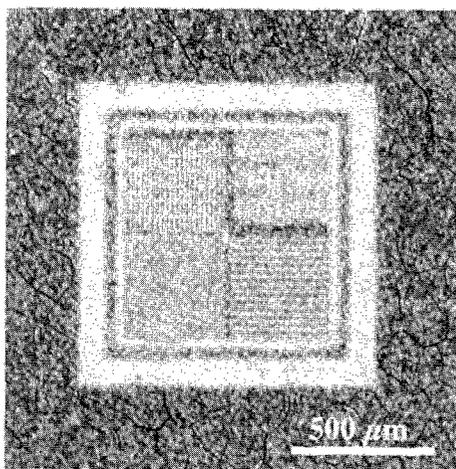
Fig. 6 Dark-field optical microscope photograph of a MPS film deposited for 5 hours on a photopatterned ODS-SAM.

4. Conclusion

MPS films were synthesized through organized cationic surfactant templating on two of the substrate surfaces on which functional groups were molecularly defined, that is, one was a hydrophilic OH group and another was a hydrophobic ODS group. The morphologies of the deposited MPS on the OH and ODS terminated surfaces were quite different, showing the difference in the supramolecular template structures formed on each surface.

In addition, microstructures of the MPS film were controlled with μm-scale designs through the spatial control of surfactant-assembling using photopatterned ODS-SAM. This patterned growth of MPS will be useful for a variety of device applications.

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