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Surface morphology control of thin films prepared by solution processes and its application

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Surface morphology of materials brings various new properties to the surface, and thus, the control of the surface morphology is very important. In this paper, surface morphology control of sol–gel derived films using several processes has been reviewed. Hot water treatment (bottom up process), combination of UV-irradiation and chemical etching (top down process), and micropattern formation using a hydrophobic-hydrophilic patterned surface were reported.

1. Introduction

Formation of thin films by solution processes has been widely studied because those processes are simple and cost-effective ones and can be applied to various types of substrates with large area or curved surfaces.[1,2] Among the solution processes, the sol–gel method is extensively studied to form thin films on the substrates using precursor sol prepared by the hydrolysis and condensation reactions of metal alkoxides or inorganic compounds.[1] By control of the reaction, rather thick films or nano-structured thin films can be obtained by the sol–gel process.

On the other hand, it is well known that the surface morphology of materials brings various new properties to the surface, and the control of the surface morphology is very important. For example, wettability of solid surfaces with liquids is governed not only by the chemical properties but also the microstructure of the surfaces,[3] and a hydrophobic surface with small roughness often shows superhydrophobic property. Reflection of surface is also affected by the surface roughness. The cornea of moth's eye has the periodic fine structure smaller than wavelength of visible light, and has anti-reflective (AR) properties.[4]

For the control of surface morphologies, "top down processes", such as physical or chemical etching of the surface or embossing of soft materials formed on the surface, are often used. The scale of the periodic structures in these techniques is often limited by the laser wavelength because those structures or photomasks or stamper for those structures are usually produced by using interference fringes generated by laser beams. Another approach to control of surface morphologies is "bottom up process", such as the formation of nano-crystals on the surface through a solution process. By controlling the precipitation process, nano-structured surface, which cannot be obtained by top down processes, can be realized.

In this paper, three topics for the the surface morphology control of sol–gel derived thin films using various processes such as hot water treatment (bottom up process), combination of UV-irradiation and chemical etching (top down process), and

micropattern formation using a hydrophobic-hydrohpilic patterned surface are reported.

2. Formation of nano-structured thin films by a hot water treatment

We found that nano-structured alumina-based oxide thin films can be obtained by a hot water treatment of sol–gel derived precursor films.[5]–[13] Nanocrystals, such as bohemite (AlOOH),[5]–[8] Zn–Al,[9),10),12)] Mg–Al[11)] Ni–Al[13)] layered double hydroxide (LDH) were found to be precipitated on the surface by the hot water treatment of the precursor films, and these nano-structured thin films have been applied to superhydrophobic and/or superhydrophilic, AR, anion-exchange, and electrode coatings.

2.1 Preparation of flowerlike Al_2O_3 by hot water treatment

Nanocrystals of bohemite (AlOOH) were found to be precipitated on the surface by the hot water treatment of the precursor porous Al_2O_3 gel films. **Figure 1** shows FE-SEM images of the surface of the sol–gel derived alumina film (a) heat treated at 400°C, and (b) immersed in boiling water for 30 min, and (c) a cross section image of the immersed film.[5),6)] In Fig. 1(a), the alumina gel film without immersion shows very smooth surface. After the immersion in hot water, nanocrystals with 20 to 50 nm in size are observed as shown in Fig. 1(b), and we have named this structure as the "flowerlike structure". In this process, precursor gel films prepared by the sol–gel process were immersed in hot water under the ambient atmosphere at temperatures less than 100°C. Most of studies on oxide or hydroxide film formation from solution are usually based on the precipitation of crystals from a saturated solution of precursor, but in the present process, precursor amorphous thin films prepared by the sol–gel process are immersed in hot distilled water to form nanocrystals on the surface of the thin films.

The photograph of the cross-section of the film with the immersion showed that the structure was only formed near the surface.[5)] From the X-ray diffraction measurements of the alumina gel powders heat-treated at 400°C and immersed in boiling water, it was found that the boehmite nanocrystals are precipitated by this process.[5)] Thus, the flowerlike structure,

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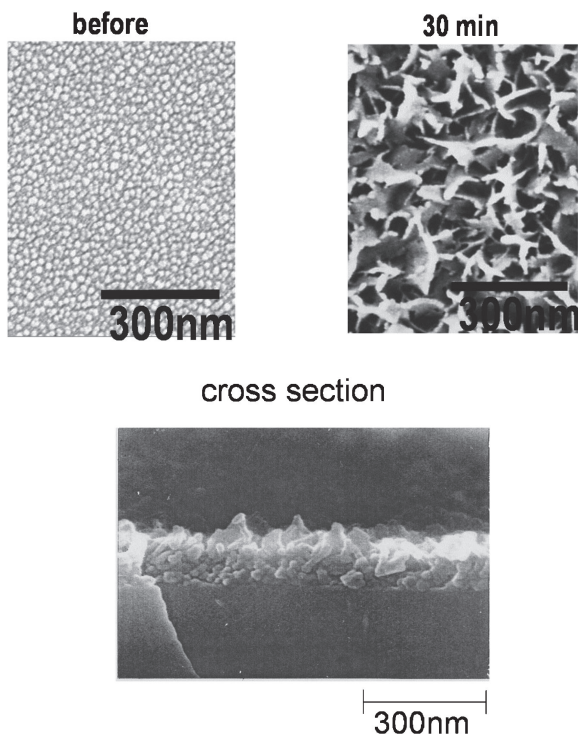
before **30 min**

cross section

Fig. 1. FE-SEM images of the surface of the sol–gel derived alumina film (a) heat treated at 400°C and (b) immersed in boiling water for 30 min, and (c) cross section of the immersed film.

Fig. 3. A photograph of a water droplet with about 1 mm in diameter on the FAS coated alumina film with flowerlike structure on a glass substrate
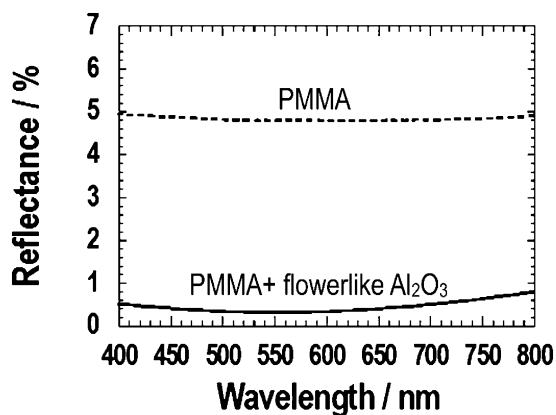

Fig. 2. Reflection spectra of the bare PMMA substrate and that coated with flower like alumina.

which consists of boehmite, is supposed to be formed with the dissolution-reprecipitation process by the reaction between sol–gel derived porous Al_2O_3 films and with H_2O. Formation process of the flowerlike alumina will be discussed in Section 2.4.

We also found that the preheat treatment at 400°C was unnecessary for the formation of the flowerlike structure with hot water treatment and the maximum process temperature was successfully lowered from 400 to 60°C.[7),8)]

2.2 Anti-reflective properties of flowerlike alumina thin films on the glass substrates

We found that flowerlike alumina thin films show excellent antireflective (AR) properties in the wide visible light wavelength region on glass substrates,[14),15)] and polymer substrates.[16),17)] As an example, **Fig. 2** shows the reflection spectra of the bare
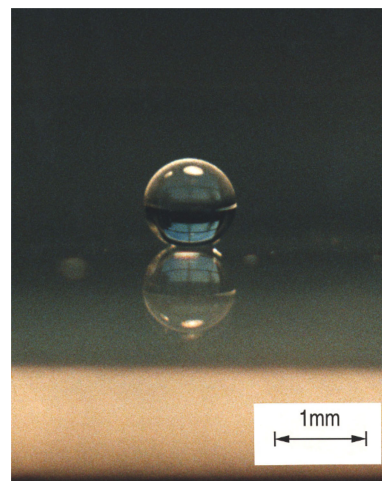
PMMA substrate and that coated with flower like alumina.[16)] The reflectance of the coated substrate was less than 0.5% from 300 to 720 nm. The transmittance spectra of the coated substrate showed high transparency in visible light region, indicating that almost no light scattering occurred with the flowerlike alumina. In the usual mono- or multi-layered AR films, the AR properties usually show large incident angle dependence. However, the AR effects based on the small roughness in this study, which is similar to the effects by the so-called moth-eye structure, showed very small incident angle dependence.[17)] Canon Inc. applied this coating to the inside surface of the camera lens, where we could not touch the coated part. They call this coating the "subwavelength structure coating" abbreviated as SWC.[18)] They succeeded in commercializing camera lens with SWC in 2009.

2.3 Application of flowerlike alumna to superhydrophobic coating films

Wettability of the surface can be changed by the control of surface free energy of a solid surface. Heptadecafluorodecyltrimethoxysilane, which is one of fluoloalkylsilane (FAS), was used as a chemical agent with low surface free energy. Partially hydrolyzed FAS was coated on the alumina films with the flowerlike structure. **Figure 3** shows a photograph of a water droplet with about 1 mm in diameter on the FAS coated alumina film with flowerlike structure on a glass substrate.[5)] This surface shows extremely high water repellency with contact angle for water of about 165°. UV visible spectrum of the substrates coated with the film showed a transmittance higher than 92% in the visible range. The contact angle for water was 110° for FAS-coated substrates without the flowerlike under layers, indicating that the water repellent properties are further enhanced by the roughness with 20 to 50 nm.

Similarly we have succeeded in preparing transparent, superhydrophobic coating films on poly(ethylene terephthalate) (PET) substrates at low temperatures around 60°C through this process.[7),8)]

2.4 Formation process of flowerlike alumina

To clarify the formation process of flowerlike alumina, NaCl, $MnCl_2$, ethanol and ethylene glycol was added to the hot water, and effects of these additives were studied.[19)] To evaluate the degree of the nanocrystal formation, the hot-water treated samples
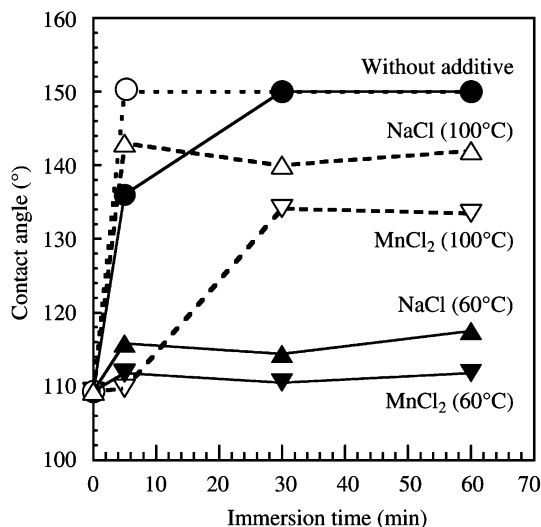
Fig. 4. Immersion-time dependence of the contact angle for water on FAS-coated alumina gel films immersed in hot water with 0.2 M NaCl and MnCl$_2$.

were coated with fluroalkylsilane, and the contact angle for water was measured. If enough amounts of nanocrystals are formed, the surface gives a large contact angle due to the enhancement of hydrophobic property by the small roughness, as described above.

Figure 4 portrays the immersion-time dependence of the contact angle for water on alumina gel films immersed in hot water with added inorganic salts, 0.2 M NaCl and MnCl$_2$. Without adding salts, the contact angle reaches about 150° with the hot water treatment. At 60°C, the contact angle on the surface of the gel film immersed in water with NaCl or MnCl$_2$ does not change during hot water treatment for up to 60 min: the surface remains smooth during the hot water treatment. On the surface immersed in water with NaCl and MnCl$_2$, at 100°C, the contact angles, respectively, reach about 140 and 135°. These results indicate that the addition of inorganic salts, as well as a decrease in the hot water treatment temperature, both diminish the growth of the boehmite nanocrystals on the surface during the hot water treatment.

It has been reported that the solubility of boehmite crystals in water increases concomitantly with increased ionic strength of the solution.[20] Lefevre et al.[21] revealed that immersion of γ-alumina in water for long durations engenders formation of bayerite [β-Al(OH)$_3$]. It is known that gibbsite readily dissolves at moderate hydroxide concentrations and moderate temperatures, while boehmite dissolution requires more rigorous conditions and generally is kinetically slow. Gong et al.[22] found that gibbsite [α-Al(OH)$_3$] dissolved into a basic solution with sodium hydroxide and then crystallized as boehmite. Consequently, in the pseudoboehmite nanocrystal formation process of the present study, alumina constituents in the precursor amorphous gel film first dissolve in water. Then pseudoboehmite (Al$_2$O$_3$·H$_2$O) nanocrystals, which are stable at temperatures from 60 to 100°C and have small solubility, are presumed to be re-precipitated from the solution because of the supersaturation in the immediate vicinity of the film surface. Addition of inorganic salts in water, which increases the ionic strength, increases the solubility of boehmite and, consequently, diminishes the precipitation of pseudoboehmite. Addition of ethanol or ethylene glycol to the hot water also diminished the growth of boehmite nanocrystals during the hot water treatment. Addition of ethanol or ethylene glycol to water
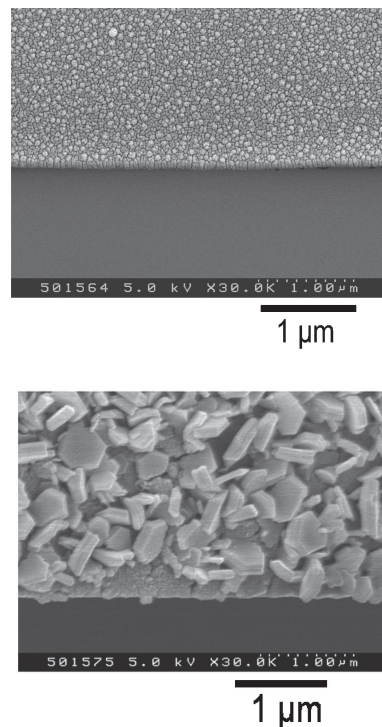

Fig. 5. FE-SEM image of the surface of the Al$_2$O$_3$–ZnO films, heat-treated at 400°C and immersed in hot water for 15 min.

must decrease the solubility of alumina in these solutions, and thus, the precipitation of nanocrystals was diminished.

2.5 Formation of layered double hydroxide nano-crystals by a hot water treatment

Layered double hydroxides (LDHs) are anionic clays consisting of positively charged metal hydroxide layers with anions located in the interlayer for charge compensation of the cationic layers. The chemical formula for LDHs is [M$^{II}_{1-x}$M$^{III}_x$(OH)$_2$]$^{x+}$-(A^{n-})$_{x/n}$·mH$_2$O, where M^{II} is a divalent metal cation, M^{III} is a trivalent cation, and A^{n-} is an anion. Because of their potential application as anion exchangers, catalysts, electrochemical sensors and bio-active materials, LDHs have received increasing attention in recent years.[23]–[25] LDHs are typically prepared using co-precipitation processing and are obtained as powder. However, for application of LDH to functional materials and for evaluation of their optical properties or intercalation reaction of LDH crystals, formation of LDH thin films on substrates is favorable.

We have successfully prepared Zn–Al LDH precipitated films directly on glass substrates through the sol–gel method with a hot water treatment.[9],[10] Al$_2$O$_3$–ZnO amorphous thin films were prepared as a precursor film. **Figure 5** shows FE-SEM image of the surface of the Al$_2$O$_3$–ZnO films, heat-treated at 400°C, and immersed in hot water for 15 min.[9] Before the hot water treatment, the surface of the film was smooth as shown in Fig. 5(a). As shown in Fig. 5(b), nanocrystals with hexagonal structure are formed after the hot water treatment. The nanocrystals were large enough to cause the scattering of the visible light, and the film turned opaque after the hot water treatment. The XRD patterns of the film showed that the nanocrystals formed on Al$_2$O$_3$–ZnO films were Zn–Al LDH intercalated with carbonate ions.[9]

In the present process, however, the precursor film was amorphous, and during hot water treatment, the Al and Zn sources

seem to be dissolved from the amorphous film on the substrate. Then, the ion species immediately diffuse and nucleate at the surface of the film. Thus the nanocrystals are thought to grow by a dissolution-reprecipitation process, which must be different from the calcinations-rehydration process in LDH powders reported so far.

With the similar process, we found that Mg–Al LDH,[11] Ni–Al LDH and Co–Al LDH[13] precipitated thin films were easily obtained with the hot water treatment. In addition, Zn–Al LDHs intercalated with several organic anions were found to be easily obtained by immersion of precursor thin films in the water containing organic anions.[12),26)]

3. Patterning of sol–gel derived thin films by the combination of UV-irradiation and chemical etching (top down process)

Fine patterning techniques of sol–gel derived films have attracted much attention for the practical applications of these films to devices like integrated optical circuits and micro-electronic memories. One approach to generate finely patterned oxide thin films is embossing of sol–gel derived thin films.[27] Another approach is utilization of the effects of UV lights on photosensitive precursor gel films. In the sol–gel method, interaction with UV light can be achieved by incorporation of photosensitive organic group in the starting materials. A fine patterning process for oxide thin films, in which the irradiation of UV-light on the gel films from chemically modified metal alkoxides led to the change of solubility of these gel films in acidic solution or alcohol, has been reported.[28] For the preparation of planar waveguides, photosensitive inorganic–organic hybrid coating films prepared by the sol–gel method have been studied extensively.[29] In these studies on inorganic–organic hybrid coating films, trimethoxysilylpropylmethacrylate (TMSPM) has been favored as a precursor since the methacrylate group easily polymerizes under UV irradiation or thermal treatment,[29),30)] and the polymerization leads to an increase of refractive index to control waveguiding. We have reported that the preparation of inorganic–organic hybrid coating films from vinyltriethoxysilane (VTES), allyltriethoxysilane or TMSPM, and zirconium n-tetrapropoxide modified with methacrylic acid,[31] and found that patterns with a width of about 10 μm and thickness of about 15 μm were formed by the etching of unirradiated region of the films. For the application of those hybrid films to waveguides, thicker films without cracks and smaller organic content should be prepared. We also found that inorganic–organic hybrid thick coating films, the maximum thickness of which was about 40 μm, prepared from only hydrolyzed vinyltriethoxysilane (VTES) was patternable with UV-irradiation. With UV irradiation from a high-pressure mercury lamp through a photomask on the hybrid films, solubility of the films in alcohol or alkaline solution was found to be decreased. **Figure 6** shows SEM images of micropatterns prepared using VTES on silica substrates. The thickness of the coating film before UV irradiation and leaching is about 40 μm. Rectangular columns with edges of about 20 μm and height of about 40 μm were formed by the etching of unirradiated region of the films with an alkaline solution. In the formation of hybrid films, Si–O–Si network is formed during the hydrolysis and condensation process, and the siloxane network could be the steric hindrance for the polymerization of vinyl group. However, the IR, Si–NMR, hardness, and solubility results showed that depletion and polymerization of C=C bonds did occur by UV irradiation, suggesting that vinyl groups should form microdomains in the hybrids. Vinyl groups in the microcomeains are supposed to be polymerized by the
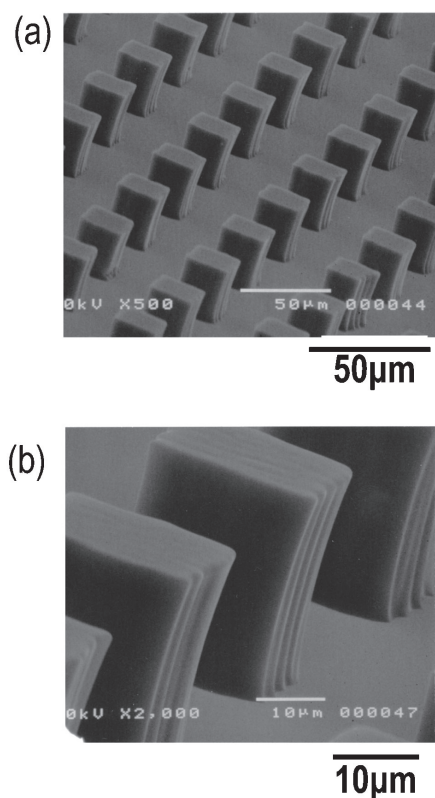
Fig. 6.   SEM image of micropatterns prepared using VTES on silica substrates.

UV-irradiation, and formation of organic network must lead to the increase in the hardness and the decrease in solubility for the alkaline solution. The achievement of such large height in the micropatterns suggests the possible practical application of VTES-derived films to the microptical components such as waveguides and photonic crystals.

4. Micropatterning of oxide thin films using hydrophobic-hydrophilic patterned surface

The most common approach to generate fine patterned oxide thin films is the irradiation of UV light on photosensitive precursor gel films. However, as a different approach for micropatterning, micropatterning of oxide thin films using patterned self-assembled monolayers has also been reported.[33),34)] We have proposed an approach to form convexly shaped oxides micropattern by using superhydrophobic/superhydrophilic or hydrophobic/hydrophilic patterned surfaces.[35)–41)]

We found that superhydrophobic-superhydrophilic micropatterns were easily obtained by conversion of the superhydrophobic surface into superhydrophilic using UV-irradiation.[35),36)] The three layered coating film, which consists of a flowerlike alumina layer, a very thin TiO_2 gel layer and a FAS layer, showed superhydrophobic property; the contact angles for water on these three layered films were about 150°. After UV light irradiation from a high-pressure mercury lamp, the contact angle for water on the three layered coating films became less than 5°. These results indicate that the fluoroalkyl chain of FAS was cleaved by the irradiation of UV light through the photocatalytic reaction on TiO_2 layer. With the cleavage of the fluoroalkyl chain, the FAS layer became a silica layer, and the fine roughness in flowerlike
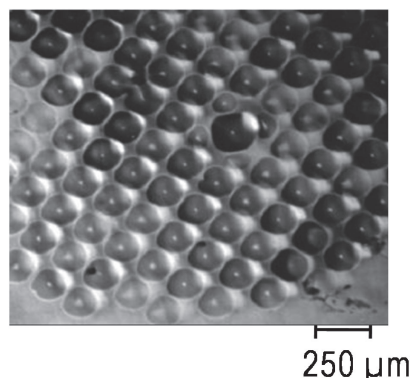
Fig. 7. Optical microscope photograph of water droplets on the super-hydrophobic-superhydrophilic surface prepared by the irradiation of UV light through a photomask.

Table 1. Patternability of various metal oxide precursor sols prepared from metal alkoxides on hydrophobic-hydrophilic patterned surfaces

Metal oxide precursor solution	Patternability
$Si(OEt)_4+EtOH+H_2O$	○
$Zr(O\text{-}n\text{-}Pr)_4+i\text{-}PrOH+EAcAc+H_2O$	×
$Al(O\text{-}sec\text{-}Bu)_3+i\text{-}PrOH+EAcAc+H_2O$	×
$Ti(O\text{-}n\text{-}Bu)_4+EtOH+AcAc+H_2O$	×

○: Liquid could be patterned. ×: Liquid could not be patterned.

Fig. 8. Optical photograph of zirconia micropattern formed on the hydrophobic-hydrophilic patterned surface using the precursor solution from $ZrOCl_2$

Table 2. Patternability of various metal oxide precursor solutions prepared by metal chloride or oxychloride on hydrophobic-hydrophilic patterned surfaces

Metal oxide precursor solution	Patternability
$AlCl_3+EtOH$	○
$ZrCl_4+EtOH$	○
$ZrOCl_2+EtOH$	○
$TiCl_4+EtOH$	○
$SnCl_2+EtOH$	○

○: Liquid could be patterned. ×: Liquid could not be patterned.

Al_2O_3 enhances the hydrophilic property of silica to super-hydrophilicity.[35]

By irradiation of UV-light through a photomask on the super-hydrophobic surface, well-defined superhydrophobic and super-hydrophilic regions were formed. **Figure 7** shows the optical microscope photograph of water droplets on the superhydro-phobic-superhydrophilic surface prepared by the irradiation of UV light through a photomask.[35] When water was put on this surface, water droplets are preferentially present in the hydro-philic areas. Since the difference of the contact angle is larger than 150°, a large volume of water can be present only on the superhydrophilic regions without bridging the other superhydro-philic regions. We found that the convexly shaped SiO_2 micro-pattern can be prepared by using this superhydrophobic-super-hydrophilic patterned surface.[37]

Since the superhydrophobic surface is rather small oil repellency, the application of superhydrophobic-superhydrophilic surface to the formation of oxide thin films by usual sol–gel precursors was rather difficult. Thus, hydrophobic-hydrophilic patterned surface was prepared.[38),39] The two layered coating film which consists of a thin TiO_2 gel layer and a FAS layer showed hydrophobic property; the contact angles for water on these two layered films were about 110°. After UV light irradia-tion from a high-pressure mercury lamp, the contact angle for water on the two layered coating films became less than 5°. By irradiation of UV-light through a photomask on the hydrophobic surface, well-defined hydrophobic and hydrophilic regions were formed.

Table 1 shows the patternability of various metal oxide pre-cursor sols prepared from metal alkoxides, on hydrophobic-hydrophilic patterned surfaces.[38] Precursor sol from tetraethoxy-silane can be only patterned; silica thin films were formed only on the hydrophilic regions of the pattern. The sol from zirconium, aluminum and titanium alkoxides cannot be patterned; thin film
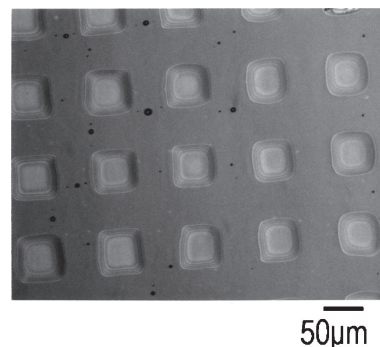
was formed over a whole area of the hydrophobic-hydrophilic patterned surface.

Table 2 shows patternability of various metal oxide precursor solutions prepared from metal chloride or oxychloride, on hydrophobic-hydrophilic patterned surfaces.[38] When metal chlo-ride or oxychloride were used as a starting material, the precursor solutions can be patterned.

Figure 8 shows the optical photograph of zirconia micro-pattern formed on the hydrophobic-hydrophilic patterned sur-face using the precursor solution from $ZrOCl_2$.[38] The zirconia micropattern shown in Fig. 8 was prepared using a 65 μm mesh as a photomask. The solution using $ZrOCl_2$ was coated only on the hydrophilic regions of the pattern, and convexly shaped zirconia micropatterns were formed without cracks after the heat-treatment at 200°C. In each pattern, the same number of inter-ference fringes was observed, meaning that each pattern has the shape of a convex lens with almost the same shape and height. The height of the pattern in this study is about 1.5 μm. The thickness of the pattern can be controlled by the spin speed or concentration of the precursor solution. This patterning technique potentially has a wide variety of applications such as fabrication of micro-optical components and finely patterned transparent electrodes.

We also applied the hydrophobic-hydrophilic patterned surface to the micropatterning of phenylsilsesquioxanes, where phenyl-silsesquioxane particles were electrophoretically deposited on Indium Tin Oxide (ITO) coated substrates with a hydrophobic-hydrophilic patterned surface.[40),41]

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