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Micropatterning of anatase TiO_2 thin films from an aqueous solution by a site-selective immersion method

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Micropatterning of anatase TiO_2 thin films by site-selective immersion was realized using a self-assembled monolayer (SAM) which has a pattern of hydrophilic and hydrophobic surfaces. A solution containing a Ti precursor contacted the hydrophilic surface during the experiment and briefly came into contact with the hydrophobic surface *via* our newly developed method. The solution on the hydrophilic surface was replaced with a fresh solution by the continuous movement of bubbles. Thus TiO_2 was deposited and a thin film was grown selectively on the hydrophilic surface. A TiO_2 thin film fabricated by the site-selective immersion method has no cracks and the feature edge acuity of its micropattern was much higher than that of the micropattern obtained by the lift-off process.

Introduction

Titanium dioxide (TiO_2) thin films are of interest because of their use in various applications including microelectronics,[1] optical cells,[2] solar energy conversion,[3] highly efficient catalysts,[4] microorganism photolysis,[5] antifogging and self-cleaning coatings,[6] gratings,[7] gate oxides in MOSFET (metal-oxide-semiconductor field effect transistor).[8,9] Accordingly, fabrication of thin films and micropatterning of TiO_2 by several methods have been attempted.

TiO_2 films have been prepared from solutions *via* a number of methods.[10–17] Deki *et al.*[10] prepared anatase type TiO_2 thin films on glass substrates from $(NH_4)_2TiF_6$ aqueous solution, adding H_3BO_3 as an F^- ion scavenger. The films were made of polycrystalline particles whose sizes were smaller than the wavelength of visible light. In this manner transparent anatase TiO_2 films were fabricated at a low temperature (25 °C) from an aqueous solution. Rutile TiO_2 thin films (0.18 μm) were also prepared on α-Al_2O_3 substrates by hydrothermal treatment of a mixed TiO_4^{2-} (0.5 M) and HNO_3 (2.0 M) solution at low temperatures (100–200 °C).[11] The film, consisting of short columnar grains (50 × 20 nm^2), was uniform, homogeneous and without visible defects. Lin *et al.*[12] synthesized amorphous TiO_2 gel films on the SAM (self-assembled monolayer) of octadecyltrichlorosilane (OTS) using $Ti(OC_3H^i_7)_4$-derived TiO_2 sols. The OTS-SAM induced precipitation of the anatase phase at the rather low temperature of 200 °C and accelerated anatase-to-rutile phase transformation when a mole ratio of H_2O : $Ti(OC_3H^i_7)_4$ as low as 0.5 was used for sol preparation. TiO_2 thin films were also deposited in aqueous HCl solutions of $TiCl_4$ for 2 h at 80 °C on SAMs of SO_3H groups formed on glass substrates.[13] $TiCl_4$ was hydrolyzed in an aqueous solution to produce TiO_2 particles that adhered to the substrate. The films consisted of TiO_2 crystallites of around 120 nm in size.

Micropatterning of TiO_2 was attempted by a number of methods using to these thin film fabrication processes.[18–23] We fashioned an anatase type TiO_2 thin film micropattern on a patterned SAM. Phenyltrichlorosilane (PTCS)-SAM was irradiated with ultraviolet light through a photomask to form an OH/phenyl micropattern which was used as a template.[18] Anatase type TiO_2 thin films were deposited over the entire area of the patterned SAM from $(NH_4)_2TiF_6$ aqueous solution with added H_3BO_3 at 50 °C for 6 h. The thin films on phenyl regions were then peeled off by sonication. Thin films on the OH group region showed strong adhesion to the OH groups compared with those on the phenyl regions. Consequently, a micropattern of anatase TiO_2 was fabricated at low temperature. However, the lift-off process causes a deterioration in the feature edge acuity of the micropattern, and a site-selective deposition process is needed to fabricate a micropatterned TiO_2 thin film which has high feature edge acuity.

Patterned TiO_2 thin films were also deposited from 0.5 M $TiCl_4$ aqueous solution in 6 M HCl at 80 °C for 2 h.[19] Regions of the SAM containing sulfonate surface functionality were produced *via* photo-oxidation (UV light 254 nm) through a mask of initially deposited thioacetate groups. During aqueous deposition of TiO_2 onto such engineered substrates, nanocrystalline anatase TiO_2 particles were deposited on the sulfonate groups of the monolayer. TiO_2 particles were selectively deposited, with a micropattern formed at a low temperature. However, the thin film consisted of particles nucleated and grown in the solution, thus lowering the film uniformity.

Tremel and co-workers[20] have prepared a TiO_2 micropattern in which gold-coated glass slides were patterned by stamping using hexadecanethiol SAMs. Using thiol terminated with a styrene monomer, micropatterns (polystyrene/hexadecane) were formed on the surface by graft polymerization of styrene. These patterned gold slides were then used as a template for TiO_2 precipitation from ethanolic solutions of $Ti[OCH(CH_3)_2]_4$ (titanium isopropoxide) with additional water vapor. TiO_2 was precipitated across the template after immersion in the solution at room temperature for 10 h. Following polymer cleavage, TiO_2 over polystyrene was removed, and a patterned TiO_2 having a feature edge acuity better than 1 μm was thereby obtained. Unfortunately, the deposited TiO_2 film displayed many cracks and TiO_2 particles. Improvement of feature edge acuity is mandatory if these patterns are to be applied to electrical or optical devices.

We recently reported selective deposition of amorphous TiO_2 thin films[21–23] using titanium dichloride diethoxide (TDD) on a patterned SAM[18,24–27] of octadecyltrichlorosilane (OTS). TiO_2 was deposited on OH group regions selectively from TDD solution[21,23] or TDD vapor[22] and produced micropatterns of TiO_2. However the micropattern must be heated to 400 °C to obtain a micropattern of anatase TiO_2 thin film for applications such as photocatalysts or photonic crystals.

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In this treatise site-selective immersion was realized using a SAM having a pattern of hydrophilic and hydrophobic surfaces. In the experiment a solution containing a Ti precursor contacted the hydrophilic surface, and briefly came in contact with the hydrophobic surface *via* our new method. The hydrophilic surface solution was replaced with a fresh solution by continuous movement of bubbles, thus TiO_2 was deposited and a thin film was grown on the hydrophilic surface selectively.

Experimental

SAM preparation

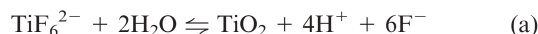
OTS-SAM and HFDTS (heptadecafluoro-1,1,2,2, tetrahydrodecyltrichlorosilane)-SAM were prepared by immersing the Si substrate (P-type Si [100]) in an anhydrous toluene solution containing 1 vol% OTS or HFDTS, respectively, for 5 min under a N_2 atmosphere.[18,21–26] The substrates with SAMs were baked at 120 °C for 5 min to remove residual solvent and promote chemisorption of the SAM. The molecular structure and surface potential of the HFDTS molecule are shown in Fig. 1. The calculation was performed at the Hartree–Fock/3-21G(*) level utilizing the SPARTAN program (SPARTAN '02 for Windows, Wavefunction, Inc.).[28] The geometry of the HFDTS molecule was optimized and the electrostatic potential was described in terms of an isoelectron density plane. The distance between fluorine at the end of the molecule and the silicon was calculated to be 1.3 nm and this will be the thickness of the HFDTS-SAM.

The SAMs on silicon substrates used as templates for site-selective deposition were exposed for 2 h to UV light (184.9 nm) (low-pressure mercury lamp, NL-UV253, Nippon Laser & Electronics Lab.) through a photomask. The SAMs were kept 150 mm from the light source in air. UV-irradiated regions became hydrophilic owing to OH group formation, while the non-irradiated part remained unchanged. Formation of a HFDTS-SAM and its modification to give OH groups by UV irradiation was verified using the water drop contact angle (θ_w) (Fig. 1). Thus, in this experiment, OH groups were formed from HFDTS-SAM by UV irradiation for 2 h.

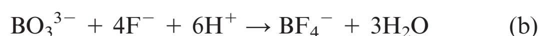
OTS-SAM has a methyl group at the end of a long methylene chain, HFDTS-SAM has a CF_3 group at the end of a $(CF_2)_7(CH_2)_2$ chain. Initially deposited HFDTS- and OTS-SAMs had water contact angles of 115° and 96°, respectively. However, UV-irradiated surfaces of both SAMs were wetted completely (contact angle < 5°).

Deposition of TiO_2 thin films

Ammonium hexafluorotitanate ($[NH_4]_2TiF_6$) and boric acid (H_3BO_3) were separately dissolved in deionized water at 50 °C and kept for 12 h. An appropriate amount of HCl was added to the boric acid solution to control the pH, and the ammonium hexafluorotitanate solution was added.[18] The solution containing 0.05 M $(NH_4)_2TiF_6$ and 0.15 M (H_3BO_3) at pH 1.5 or 2.8 was kept at 50 °C and used for site-selective immersion. Deposition of TiO_2 proceeds by the following mechanism.



$$TiF_6^{2-} + 2H_2O \leftrightharpoons TiO_2 + 4H^+ + 6F^- \quad (a)$$



$$BO_3^{3-} + 4F^- + 6H^+ \rightarrow BF_4^- + 3H_2O \quad (b)$$

The solution remained clear at pH 1.5 showing a low degree of supersaturation. On the other hand, the solution at a higher pH, such as pH 2.8, becomes turbid because of homogeneously nucleated anatase TiO_2 particles caused by a high degree of supersaturation. An anatase TiO_2 thin film was formed by heterogeneous nucleation in the solution at pH 1.5, while a film was formed by heterogeneous nucleation on the substrate and deposition of homogeneously nucleated particles at pH 2.8.[18]

Results and discussion

Fabrication of a TiO_2 thin film micropattern by site-selective immersion[29]

HFDTS-SAM or OTS-SAM that have high hydrophobicity were modified by UV irradiation to obtain a pattern of hydrophobic and hydrophilic OH group surfaces (Fig. 2). Patterned SAMs were placed upside down 5 mm above the solution surface. The top clear layer of a solution containing 0.05 M $(NH_4)_2TiF_6$ and 0.15 M H_3BO_3 kept at pH 2.8 and 50 °C was used for this experiment. Several kinds of solutions were used to form a TiO_2 micropattern, but the top clear layer of the solution was found best for site-selective deposition owing to its supersaturation capability.

Dried air which was desiccated using silica gel and potassium chloride was passed for 4 h through a tube by a pump (Air pump HIBLOW SPP-6EBS, 100 V, 8.5 W, Takatsuki Denki Co., Ltd.) 20 mm below the surface of the solution. Bubbles several millimeters in diameter were generated and moved across the surface of a patterned SAM. The solution was repelled and moved quickly across the hydrophobic surface, while the hydrophilic surface was wetted by the solution. The solution remaining on the hydrophilic surface was replaced with new solution by the moving bubbles. Consequently, the hydrophilic surface was continuously wetted with solution, while the hydrophobic surface was covered with solution for only a short time. TiO_2 was deposited on the hydrophilic surface from the solution but not on its hydrophobic counterpart. Thus site-selective immersion[28] was attained and the differences in immersion times of the two types of surfaces caused site-selective deposition of a TiO_2 thin film.

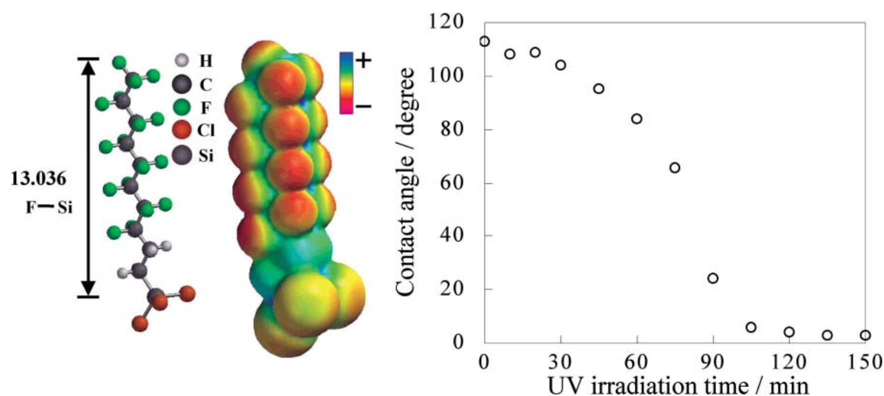


Fig. 1 Molecular structure of HFDTS and the water drop contact angle for HFDTS-SAM as a function of UV irradiation time.

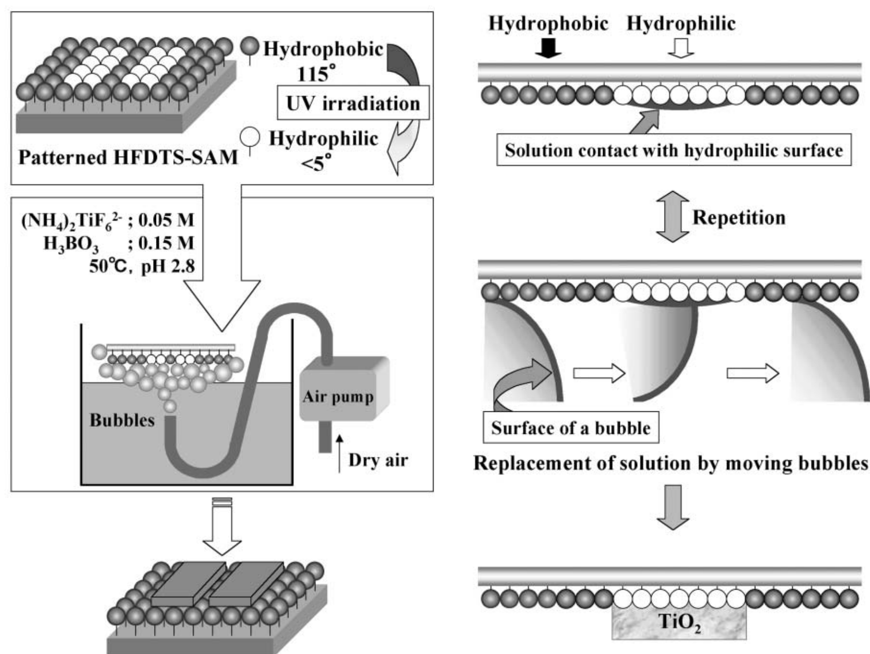


Fig. 2 Conceptual process for site-selective immersion to fabricate a micropattern of anatase TiO_2 thin film from an aqueous solution.

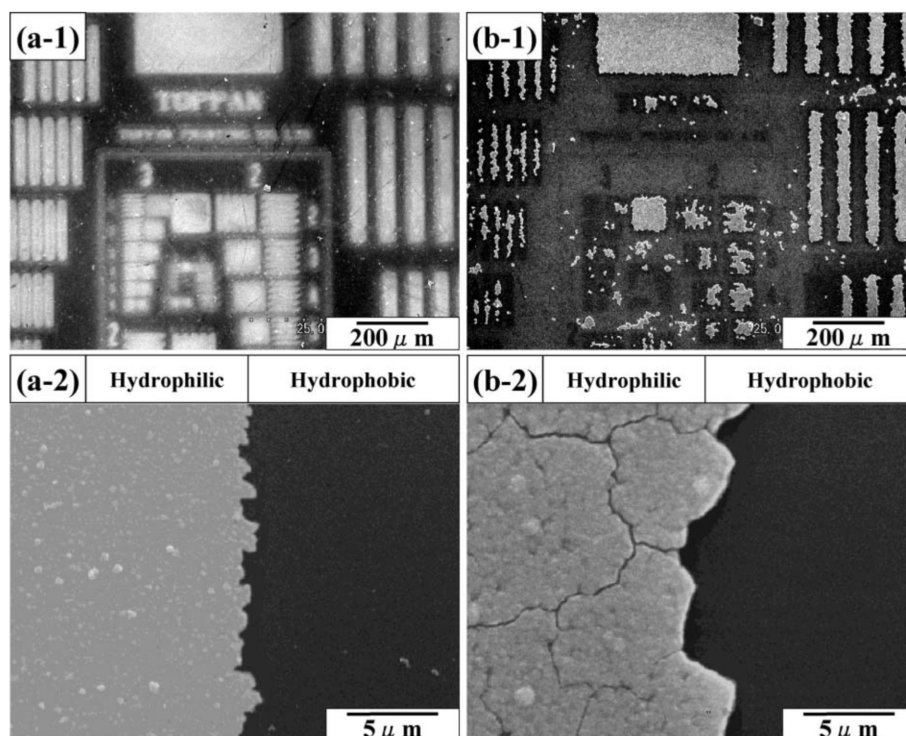


Fig. 3 SEM micrographs of micropatterns of TiO_2 thin films on a HFDTS/OH-patterned SAM fabricated by (a) site-selective immersion or (b) the lift-off process.[18]

The feature edge acuity of the micropattern fabricated on a patterned HFDTS-SAM by site-selective immersion [Fig. 3(a)] was estimated from scanning electron microscope (SEM; S-3000 N, Hitachi, Ltd.) images to be 11% and is much better than that of the pattern fabricated *via* the lift-off process[18] [Fig. 3(b)]. Their thicknesses were 1.3 μm [Fig. 3(a)] and 4.3 μm [Fig. 3(b)], respectively. Furthermore, cracks were not observed in the thin films and a smooth surface was obtained (Fig. 3[a]). Deposited films showed an XRD pattern of anatase type TiO_2 and its orientation was similar to that of films deposited in solution[18] (Fig. 4).

Surface roughness (RMS) was estimated using an atomic force microscope (AFM; Nanoscope E, Digital Instruments) image (Fig. 5) using the equation:

$$\text{RMS (standard deviation)} = [\Sigma(Z_\text{i} - Z_\text{ave})^2/n] \qquad \text{(c)}$$

where Z_i is the height at point "i", Z_ave is the average of height Z and n is the number of data points. The AFM image shows the film roughness to be 43.7 nm, with the film thickness near the edge greater than at the interior.

When a TiO_2 thin film micropattern was also formed on OTS-SAM instead of HFTDS-SAM from the same solution, its feature edge acuity was lower than that of the micropattern generated on patterned HFDTS-SAM. OTS-SAM, which has low hydrophobicity compared with HFDTS-SAM, cannot

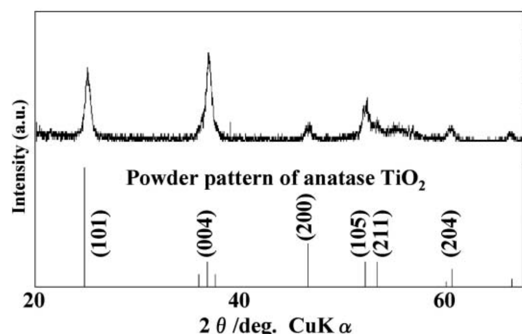


Fig. 4 XRD pattern of anatase type TiO_2 deposited on OH groups. Randomly oriented powder pattern for anatase (JCPDS Card No. 21-1272) is shown for comparison.

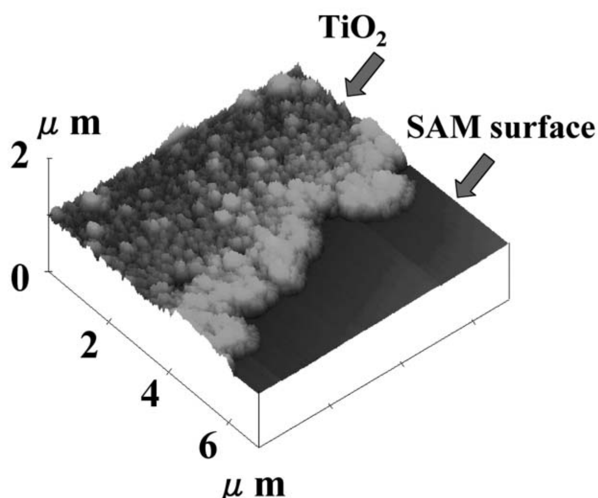


Fig. 5 AFM image of the micropattern of TiO_2 thin film on a HFDTS/OH-patterned SAM fabricated by site-selective immersion.

repel enough solution and so suppress TiO_2 deposition. This indicates a pattern possessing a highly hydrophilic surface and a highly hydrophobic surface would satisfy the requirements for a template to realize site-selective immersion *via* our method.

Additionally, patterned HFDTS- and OTS-SAMs were immersed in a solution containing 0.05 M $(NH_4)_2TiF_6$ and 0.15 M H_3BO_3 at pH 1.5 or pH 2.8 at 50 °C without using the site-selective immersion method. TiO_2 thin films were deposited on the entire area of patterned SAMs. HFDTS- and OTS-SAMs showed a water contact angle of 20–50° after immersion for 1 h. SAM hydrophobicity is decreased by nucleated or adhered TiO_2 particles, and fails to repel enough solution. One probable cause is that pinholes and other defects in the films provide water at least some degree of access to underlying unreacted OH groups in the HFDTS and OTS films. Once exposed to the solution, these sites can act as nucleation points for TiO_2 growth. Because the depositions are carried out at elevated temperatures, it is likely that pinholes and defects will continually appear and disappear on the HFTDS and OTS film surfaces due to the thermal motion of alkyl chains in these films. The TiO_2 precursors formed in these defects would contribute to the decreased hydrophobicity and act as points for eventual growth of TiO_2 over the entire SAM-covered region. This would provide a weakly bound TiO_2 film on the HFDTS and OTS regions due to the limited number of connections to the underlying silanol sites in these regions. In fact, Sagiv and others have shown that macroscopic defects induced in alkylsiloxane films can readily be accessed by solution species.[30–32] More recently, Dressick and co-workers have demonstrated that solvent accessibility to underlying substrates in aromatic siloxane films is also important[28,33,34] and may even be a greater factor in controlling the properties of those films, an observation which may account for our previous selectivity observation using phenylsiloxane films, as shown in Fig. 3(b).

Patterned HFDTS- and OTS-SAMs were placed 5 mm below the surface of the solution, putting both hydrophilic and hydrophobic surfaces in contact with the solution for an extended period of time, and TiO_2 was deposited on both. The feature edge acuity of TiO_2 thin film micropatterns (18%) was lower than that of the micropattern formed on a patterned SAM kept above the solution.

The micropattern of a TiO_2 thin film was also formed using air more humid than the dried air. However, the thin film pattern feature edge acuity (13%) was slightly lower than that obtained using dry air. Though dried air was bubbled through water and took up water molecules from the solution, it was passed through only 20 mm of solution and the humidity in the dried air bubbles would be lower than that of air. Some water molecules in air probably come into contact with the HFDTS-SAM and this decreases the hydrophobicity of the SAM. This lengthens slightly the contact time of the solution with the HFTDS-SAM and induces growth of TiO_2. The higher humidity of bubbles of air may also induce the solution to contact the hydrophobic surface so that the amount of TiO_2 deposited on the surface increases.

These experiments show that the site-selective immersion method is sensitive to the conditions of the solution and the substrate surface. In particular, surface supersaturation and hydrophobicity should be well controlled to realize site-selective immersion to fabricate micropatterns of TiO_2 thin films. Since HFDTS-SAM repels not only a water solution but also organic solvents such as toluene, the site-selective immersion method we developed can be applied to the fabrication of micropatterns of any kind so long as the film can be deposited from a solution.

Conclusions

Site-selective immersion was achieved using air bubbles which move continuously across a substrate with a hydrophilic/hydrophobic patterned surface. A micropattern of anatase type TiO_2 thin film having no cracks and high feature edge acuity was successfully fabricated by the site-selective immersion method.

References

1 G. P. Burns, *J. Appl. Phys.*, 1989, **65**, 2095.
2 B. E. Yoldas and T. W. O'Keeffe, *Appl. Opt.*, 1979, **18**, 3133.
3 M. A. Butler and D. S. Ginley, *J. Mater. Sci.*, 1980, **15**, 19.
4 T. Carlson and G. L. Giffin, *J. Phys. Chem.*, 1986, **90**, 5896.
5 T. Matsunaga, R. Tomoda, T. Nakajima and T. Komine, *Appl. Environ. Microbiol.*, 1988, **54**, 330.
6 R. Wang, K. Hashimoto and A. Fujishima, *Nature*, 1997, **388**, 431.
7 S. I. Borenstain, U. Arad, I. Lyubina, A. Segal and Y. Warschawer, *Thin Solid Films*, 1999, **75**, 2659.
8 P. S. Peercy, *Nature*, 2000, **406**, 1023.
9 D. Wang, Y. Masuda, W. S. Seo and K. Koumoto, *Key Eng. Mater.*, 2002, **214**, 163.
10 S. Deki, Y. Aoki, O. Hiroi and A. Kajinami, *Chem. Lett,*, 1996, 433.
11 Q. Chen, Y. Quian, Z. Chen, Y. Jia, G. Zhou, X. Li and Y. Zhang, *Phys. Status Solidi A*, 1996, **156**, 381.
12 H. Lin, H. Kozuka and T. Yoko, *Thin Solid Films*, 1998, **315**, 111.
13 D. Huang, Z.-D. Xiao, J.-H. Gu, N.-P. Huang and C.-W. Yuan, *Thin Solid Films*, 1997, **305**, 110.
14 K. Shimizu, H. Imai, H. Hirashima and K. Tsukuma, *Thin Solid Films*, 2000, **351**, 220.
15 W. P. Wang, Y. Yu, F. X. Hu and L. Gao, *Thin Solid Films*, 2000, **371**, 148.
16 M. K. Lee and B. H. Lei, *Jpn. J. Appl. Phys.*, 2000, **39**, 101.

17 U. Selvaraj, A. V. Prasadarao, S. Komarneni and R. J. Roy, *Am. Ceram. Soc.*, 1992, **75**(5), 1167.
18 K. Koumoto, S. Seo, T. Sugiyama, W. S. Seo and W. J. Dressick, *Chem. Mater.*, 1999, **11**(9), 2305.
19 R. J. Collins, H. Shin, M. R. DeGuire, A. H. Heuer and C. N. Shukenik, *Appl. Phys. Lett.*, 1996, **69**(6), 860.
20 M. Bartz, A. Terfort, W. Knoll and W. Tremel, *Chem. Eur. J.*, 2000, **6**(22), 4149.
21 Y. Masuda, T. Sugiyama, H. Lin, W. S. Seo and K. Koumoto, *Thin Solid Films*, 2001, **382**, 153.
22 Y. Masuda, W. S. Seo and K. Koumoto, *Langmuir*, 2001, **17**(16), 4876.
23 Y. Masuda, Y. Jinbo, T. Yonezawa and K. Koumoto, *Chem. Mater.*, 2002, **14**(3), 1236.
24 Y. Masuda, W. S. Seo and K. Koumoto, *Thin Solid Films*, 2001, **382**, 183.
25 Y. Masuda, W. S. Seo and K. Koumoto, *Jpn. J. Appl. Phys.*, 2000, **39**, 4596.
26 Y. Masuda, M. Itoh, T. Yonezawa and K. Koumoto, *Langmuir*, 2002, **18**(10), 4155–4159.
27 P. X. Zhu, Y. Masuda and K. Koumoto, *J. Colloid Interface Sci.*, 2001, **243**, 31–36.
28 W. J. Dressick, P. F. Nealey and S. L.Brandow, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2001, **4343**, 294–305.
29 Y. Masuda and K. Koumoto, *Jpn. Pat. Appl.*, 137641, 2002.
30 J. Gun and J. Sagiv, *J. Colloid Interface Sci.*, 1986, **112**, 457–472.
31 M. E. McGovern, K. M. R. Kallury and M. Thompson, *Langmuir*, 1994, **10**, 3607–3614.
32 J. Duchet, B. Chabert, J. P. Chapel, J. F. Gerard, J. M. Chovelon and N. Jaffrezic-Renault, *Langmuir*, 1997, **13**, 2271–2278.
33 W. J. Dressick, M.-S. Chen and S. L. Brandow, *J. Am. Chem. Soc.*, 2000, **122**, 982–983.
34 W. J. Dressick, M.-S. Chen, S. L. Brandow, K. W. Rhee, L. M. Shirey and F. K. Perkins, *Appl. Phys. Lett.*, 2001, **78**, 676–678.