Nano/micro-patterning of anatase TiO$_2$ thin film from an aqueous solution by site-selective elimination method

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Received 3 June 2003; revised 22 July 2003; accepted 4 August 2003

Abstract

We proposed a novel method to fabricate nano/micro-scaled patterns of thin films and successfully fabricated patterns of anatase TiO$_2$ thin films in an aqueous solution at 50 °C. The patterned self-assembled monolayer (SAM) having octadecyltrichlorosilane (OTS) regions and silanol regions was immersed in a solution containing a Ti precursor and subjected to ultrasonication for several hours. The difference in adhesion of thin films on substrates was employed for the site-selective elimination method. Heterogeneously nucleated TiO$_2$ and homogeneously nucleated TiO$_2$ particles adhering to the OTS–SAM could be easily eliminated from the substrate by ultrasonication, whereas those on silanol groups maintained their adhesion during the immersion period. TiO$_2$ can form chemical bonds such as Ti–O–Si with silanol groups, but cannot form them with octadecyl groups, resulting in the difference in adhesion, which is the essence of the site-selectivity of this method. The site-selective elimination method can be applied to fabricate nano/micro-scaled patterns in the solution by the immersion of the substrate that has regions on which depositions adhere strongly and regions on which depositions adhere weakly, enabling elimination by treatment such as ultrasonication.

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Keywords: Site-selective elimination; Site-selective deposition; Titanium dioxide; Self-assembled monolayer; Ultrasonication; Thin film; Aqueous solution; Green chemistry; Soft solution process; Green and sustainable chemistry

1. Introduction

By opting for a life of convenience, humans consume large amounts of mass (substance, raw materials) and energy. In particular, the amount of energy consumed by humans in just the past 100 years is extraordinary in relation to the long history of humankind and Earth. Such large-scale consumption is causing serious environmental changes.

From this perspective, we have been trying to develop environmentally friendly methods to fabricate nano/micro-sized functional devices such as nano/micro-patterns of functional thin films or particles with a minimum amount of energy consumption and mass in order to conserve the planet. Our goal is to fabricate nano/micropatterns of thin films from a harmless substance, in the desired position (without using the etching process and thus avoiding wastes), with a one-step process from raw material to device (or to material having the desired composition and shape) without preparation of substances, at ordinary temperatures and atmospheric pressure, in an environmentally friendly condition such as an aqueous solution. We are also trying to fabricate nano/microstructures from particles by self-assembly using the same concepts as for the patterning of thin films.

In the present production methods, many patterns of thin films are produced by photolithography and etching, in which films are deposited on entire areas of substrates and partially removed using various processes. The same methods are used in the production of many ceramic devices. Substances having the desired chemical compositions and crystal structures are prepared in the first step, and devices having the desired shapes are formed from the substances in the second step. Furthermore, many ceramic devices are produced using high temperature sintering.
By focusing our attention on nature, we can find many examples of environmentally friendly processes. Numerous creatures and plants fabricate nano/microstructures from inorganic and organic materials within their bodies under their natural living conditions [1]. We can learn many things from nature for the production of materials and devices. Bio-inspired processing and science will hopefully provide a solution to serious global problems.

Many techniques for the synthesis of ceramic thin films from aqueous solutions at low temperatures (25–100 °C) have been reported [2,3]. Originally used for sulfide and selenide thin films, such techniques have also been applied to oxides since the 1970s. Films of single oxides (e.g. transition metal oxides, In2O3, SiO2, SnO2) and multi-component films (doped ZnO, Cd2SnO4, ZrTiO4, ZrO2–Y2O3, Li–Co–O spinel, ferrites, and perovskites) have been produced. Compared to vapor-deposition techniques, liquid-deposition methods offer lower capital equipment costs, lower processing temperatures, and greater flexibility in the choice of substrates with respect to topography and thermal stability. Compared to sol–gel techniques, liquid-deposition methods offer lower processing temperatures, less shrinkage, and (being based on aqueous precursors) lower costs in addition to the potential for reduced environmental impact.

The main techniques for non-electrochemical synthesis of polycrystalline ceramic films from aqueous solutions at low temperatures, and some of the materials produced using them, are as follows [1]: (1) chemical bath deposition (CBD)—CoO, Co3O4, NiO, AgO, Ag2O, ZnO, CdO, In2O3, SnO2, Cd2SnO4; CdS, ZnS, SnS, PbS, MnS, CoS, NiS, CuS, Ag2S, As2S3, Sb2S3, Bi2S3, MoS2, and corresponding selenides. (2) Successive ion layer adsorption and reaction (SILAR)—MnO2, FeOOH/Fe2O3, NiO, Cu2O, CuO, ZnO and ZnO with Ni, Cu, or Cd doping, TiO2, SnO2, LaNbO3, CeO2, Y2O3, or Y, La and Eu hydroperoxide; ZnS, CdS, PbS, CoS, CuS, Ag2S, Sb2S3, In2S3 and Bi2Se3. (3) Electrolecless deposition (ED) with catalyst (Ag+, Sn2+ or Pb2+). (4) Liquid phase deposition (LPD)—SiO2, TiO2, ZrO2, V2O5, β-FeOOH/α-Fe2O3, NiFe2O4, LnMO3 (Ln = La, Nd; M = Cr, Mn, Fe, Co), SnO2. Liquid-phase deposition is an aqueous technique for deposition of oxide films that has been widely used for SiO2 [4,5] but is being increasingly studied as a route for films of oxides such as TiO2 [6–13] and others [2].

TiO2 thin films are of interest for use in various applications including microelectronics [14], optical cells [15], solar energy conversion [16], highly efficient catalysts [17], microorganism photolysis [18], antifogging and self-cleaning coatings [19], gratings [20], gate oxides in MOSFETs (Metal-Oxide-Semiconductor Field Effect Transistor) [21,22] and so on. Accordingly, fabrication of thin films and nano/micro-patterns of TiO2 has been attempted by several methods.

TiO2 films were prepared from solutions via various methods [6–13,22–30] and micropatterning of TiO2 was attempted by a number of methods [31–38] referring to these thin film fabrication processes. We reported the deposition of anatase TiO2 thin films from an aqueous solution and proposed novel techniques for micropatterning of the films [36–38]. A micropattern of anatase TiO2 thin films was fabricated on a patterned self-assembled monolayer (SAM) by lift-off process [10]. Phenyltrichlorosilane (PTCS)-SAM was irradiated by ultraviolet light through a photomask to form a silanol/phenyl micropattern to be used as a template. Anatase TiO2 thin films were deposited on the entire area of a patterned SAM from (NH4)2TiF6 aqueous solution with the addition of H3BO3 at 50 °C for 6 h. The TiO2 thin film thus deposited was continuous. The film was dried in air to form numerous cracks for the subsequent lift-off process. Thin films on phenyl regions were then peeled off along the cracks by sonication. Thin films on the silanol region showed strong adhesion to silanols compared to those on the phenyl regions. Consequently, a micropattern of anatase TiO2 was fabricated at low temperature. However, the lift-off process caused a deterioration of feature edge acuity of the micropattern. A novel process to realize site-selective deposition (SSD) is required for fabricating a micropattern with high feature edge acuity.

Moreover, site-selective immersion was realized using a SAM having a pattern of hydrophilic and hydrophobic surfaces [36,37]. In the experiment the solution containing a Ti precursor contacted the hydrophilic surface, and briefly came into 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 applied to fabricating micropatterns of any kind as 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.

We recently developed a novel method for SSD of thin films using a seed layer [38]. The deposition process of anatase TiO2 from an aqueous solution was evaluated in detail using a quartz crystal microbalance and the results showed that the nucleation and initial growth of anatase TiO2 were accelerated on amorphous TiO2 thin films compared with silanol, amino, phenyl or octadecyl groups. Amorphous TiO2 thin films were deposited on silanols regions of a patterned octadecyltrichlorosilane (OTS)–SAM from a titanium dichloride diethoxide solution. This substrate was immersed in an aqueous solution containing a Ti precursor contacted the hydrophilic surface, and briefly came into 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 applied to fabricating micropatterns of any kind as 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.
In this study we developed a novel method to realize SSD of thin films using a site-selective elimination method. The concept of this method is the use of the difference in adhesive strength of the depositions to the substrate. This difference, which is presumably caused by the difference in chemical bonds between depositions and substrates, was shown in previous work [10]. In this method, the patterned SAM having OTS regions and silanol regions was used as a template. The substrate was immersed in the solution containing Ti precursor and subjected to ultrasonication for several hours. Ultrasonication eliminated many deposited particles from OTS regions but not as many from silanol regions because depositions adhered strongly on silanol particles from OTS regions but not as many from silanol regions selectively to form thin films and a pattern of anatase TiO2 thin films having high feature edge acuity compared to our previous works [10,36–38] was successfully fabricated.

2. Experiment

2.1. SAM preparation

An Si wafer (p-type Si [100]) was sonicated in water, ethanol or acetone for 10 min, respectively, and exposed for 2 h to UV light (184.9 nm) (low-pressure mercury lamp, NL-UV253, Nippon Laser and Electronics Lab.) to clean the surface. The OTS–SAM was prepared by immersing the Si substrate in an anhydrous toluene solution containing 1 vol% OTS for 5 min under an N2 atmosphere [39–45] (Fig. 1). The substrate with the SAM was baked at 120 °C for 5 min to remove residual solvent and promote chemisorption of the SAM.

The SAM on the silicon substrate was exposed for 2 h to UV light through a photomask to be used as a template for SSD. UV-irradiated regions became hydrophilic due to silanol group formation, while the non-irradiated part remained unchanged. Formation of the OTS–SAM and its modification to silanol groups by UV irradiation was verified using the water drop contact angle (θw). The initially deposited OTS–SAM showed a water contact angle of 96°, but the UV-irradiated surface of SAM was wetted completely (contact angle <5°). The water contact angle of the OTS–SAM was slightly lower than the reported values (111–115°) [46,47].

Additionally, we used an old SAM for Fig. 2(b) to check the influence of pinholes and defects in the SAM for TiO2 deposition. An SAM was kept in air for 1 month after preparation and was patterned by UV irradiation. The patterned SAM, which probably had many pinholes and other defects, was then immersed in the solution to deposit TiO2 thin films.

2.2. Deposition of TiO2 thin films

Ammonium hexafluorotitanate ([NH4]2TiF6) (purity 96%, 1.031 g) and boric acid (H3BO3) (purity 99.5%, 0.932 g) were dissolved separately in deionized water (50 °C, 50 ml) (Fig. 1). An appropriate amount of HCl was added to the boric acid solution to control pH, and ammonium hexafluorotitanate solution was added [10]. Solutions (100 ml) with 0, 0.1 or 0.6 ml of HCl showed pH 3.8, 2.8 or 1.5, respectively. Supersaturation of solution can be changed by pH value as discussed in Ref. [54]. TiO2 thin films can be formed fast by the deposition of homogeneously nucleated particles at high pH condition such as pH 3.88, and uniform films can be obtained slowly by heterogeneous nucleation at low pH condition. SAMs were immersed in the solution (100 ml) containing 0.05 M (NH4)2TiF6 and 0.15 M (H3BO3) at pH 1.5, 2.8 or 3.8 and kept at 50 °C for 4 h, to deposit anatase TiO2. Ultrasonication was done during immersion period. Deposition of TiO2 proceeded by the following mechanism [6–8]:

\[
\text{TiF}_6^{2-} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 6\text{F}^- \quad (1)
\]

\[
\text{BO}_3^{3-} + 4\text{F}^- + 6\text{H}^+ \rightarrow \text{BF}_4^- + 3\text{H}_2\text{O} \quad (2)
\]

Eq. (1) is described in detail by the following two equations:

\[
\text{TiF}_6^{2-} \rightarrow \text{TiF}_6^{-n}\text{OH}^+_n + n\text{F}^- (6-n)\text{OH}^- \rightarrow \text{Ti(OH)}_6^{2-} + 6\text{F}^- \quad (3)
\]

\[
\text{Ti(OH)}_6^{2-} \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} + 2\text{OH}^- \quad (4)
\]

Fluorinated titanium complex ions gradually change into titanium hydroxide complex ions in an aqueous solution as shown in Eq. (3). Increase of F\(^-\) concentration displaces the Eqs. (1) and (3) to the left, however, produced F\(^-\) can be
scavenged by $\text{H}_3\text{BO}_3(\text{BO}_3^{2-})$ as shown in Eq. (2) to displace the Eqs. (1) and (3) to the right. Anatase TiO$_2$ was formed from titanium hydroxide complex ions (Ti(OH)$_6^{2-}$) in Eq. (4), and thus the supersaturation degree and the deposition rate of TiO$_2$ depend on the concentration of titanium hydroxide complex ions. The high concentration of $\text{H}^+$ displaces the equilibrium to the left in Eq. (1), and the low concentration of $\text{OH}^-$, which is replaced with $\text{F}^-$ ions, suppresses ligand exchange in Eq. (3) and decreases the concentration of titanium hydroxide complex ions at low pH such as pH 1.5. The solution actually remained clear at pH 1.5, showing its low degree of supersaturation. On the other hand, the solution at high pH such as pH 2.8 or 3.8 became turbid because of homogeneously-nucleated anatase TiO$_2$ particles caused by a high degree of supersaturation. Anatase TiO$_2$ thin film was formed by heterogeneous nucleation in the solution at pH 1.5, while the film was formed by heterogeneous nucleation and deposition of homogeneously nucleated particles at pH 2.8 or 3.8.

3. Results and discussion

3.1. Site-selective elimination and nano/micro-scaled pattern of thin films

After having been immersed in the solution with ultrasonic treatment, the substrates were rinsed with distilled water and observed by an optical microscope (BX51WI with CCD camera), an optical microscope (BX51WI Microscope, Olympus Optical Co., Ltd.) with a digital camera (DP50, 5.8 megapixels, Olympus Optical Co., Ltd.) and a computer for capturing data, a scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.), and a scanning probe microscope (SPI 3800N, Seiko Instruments Inc.) that was operated in AFM (atomic force microscopy) tap mode to observe the topography of the surface. AFM scans were operated at room temperature under ambient air. Thin films were observed as being dark in an optical micrograph (Fig. 2). Separated parallel lines 200–400 nm in width at 100–200 nm intervals were successfully fabricated with this method (Fig. 2(a) and (b)). The length of the separated parallel lines reached more than 100 μm (Fig. 2(a) and (b)). A cross section of the lines was shown as a semicircle, and the thickness of the center of the lines was estimated to be about 100 nm by AFM observation (Fig. 3). Feature edge acuity of the pattern was higher than that of the pattern fabricated by our lift-off process[10] or by the site-selective immersion method[36,37]. SSD was realized at any pH conditions such as pH 3.88, 2.8 or 1.5. Patterns which have higher feature edge acuity can be obtained at low pH conditions because films were formed slowly without the deposition of homogeneously nucleated particles.

For the adhesion of TiO$_2$ films to silanol groups, the pH of the deposition solution is critical. Pizem et al.[3] reported that adherent TiO$_2$ films formed from solutions similar to those used here at pH 3.9 (i.e. the pH used in the films of Figs. 2–4), but that the films were less adherent at pH 2.9. They related this difference in adherence to an increased
electrostatic attraction of TiO₂ to the oxidized surface of silicon at the higher pH. In our experiment, there also were less adherence of TiO₂ at pH 2.8 and 1.5 than that at pH 3.5 due to low supersaturation shown in Eq. (1) and low electrostatic attraction [3].

However, some depositions were observed on octadecyl group regions in Fig. 2(b). One probable cause is that pinholes and other defects in the films provide at least some degree of access of water to underlying unreacted OH groups in the OTS films. Once exposed to the solution, these sites can act as nucleation points for TiO₂ growth. Because the depositions are performed at elevated temperatures, it is likely that pinholes and defects will continually open and close on the OTS film surfaces due to thermal motions of alkyl chains in the films. The TiO₂ precursors formed in these defects would act as points for eventual growth of TiO₂ over the entire SAM-covered region. This would provide a weakly bound TiO₂ film on the OTS film regions due to the limited number of connections to the underlying silanol sites in the film regions. In fact, Sagiv and others have shown that macroscopic defects induced in alkylsiloxane films can readily be accessed by solution species [48–50]. More recently, Dressick and coworkers demonstrated that solvent accessibility to underlying substrates in aromatic siloxane films is also important [51–53] and may be an even greater factor in controlling the properties of those films, which may account for our previous selectivity observation using phenylsiloxane films, as shown in the lift-off process [10].

In the lift-off process [10], thin films were formed on the entire area of patterned SAM that has silanol group regions and phenyl (or octadecyl) group regions. After being dried, the substrate was sonicated in water to lift off thin films on phenyl (or octadecyl) group regions selectively. Thin films on phenyl (or octadecyl) group regions were peeled off along the cracks that formed during the drying process. Thin films on phenyl (or octadecyl) group regions without cracks were not peeled off because depositions strongly connected to each other to form solid timber (monolith). The lift-off along cracks decreased the feature edge acuity of the pattern in this method. Thin films were formed on silanol group regions selectively and SSD was realized with our newly developed method. This resulted in high feature edge acuity of the patterns compared to our previous works [10]. Additionally, the micropattern of thin films was also fabricated by the site-selective immersion method [36]. A solution containing a Ti precursor contacted the hydrophilic regions during the experiment and briefly came into contact with the hydrophobic regions. The solution on the hydrophilic surface was replaced with a fresh solution by continuous movement of bubbles. Thus TiO₂ was deposited and a thin film was grown on the hydrophilic regions selectively. This technique can be applied for the formation of many kinds of films from any solution and to fabricate micropatterns for many kinds of thin film because the technique creates the difference in contact time of the solution between hydrophilic regions and hydrophobic regions. However, it is difficult to form a solution layer on nano-scaled hydrophilic regions selectively and replace it with a fresh solution by continuous movement of bubbles while avoiding contact of the solution on hydrophobic regions. This prevents fabrication of nano-scaled pattern with this method. On the other hand, SSD was realized in the solution with our newly developed method using the difference of adhesive strength of depositions to substrates. Heterogeneously nucleated deposition and homogeneously nucleated particles and/or clusters can be removed from octadecyl group regions even if these regions are designed in nano-scale order in which depositions are smaller. This allowed us to realize high feature edge acuity of the patterns compared to site-selective immersion [36–38].

3.2. Characterizations of thin films

The distribution of elements on the surface of the substrates was evaluated by energy dispersive X-ray analysis (EDX; EDAX Falcon, EDAX Co. Ltd.), which is built into SEM. Titanium was detected from thin films selectively and oxygen was detected mainly from silanol group regions by EDX (Fig. 4). Other elements, except for silicon from the substrate, were not observed from the thin film and substrate by EDX. Oxygen was detected from not only the deposited thin film but also from the natural oxide layer (amorphous SiO₂ layer) formed on all surface areas of
These observations showed predominant deposition of titanium oxide on silanol group regions.

The deposited thin films were also investigated using an X-ray diffractometer (XRD; RAD-C, Rigaku) with Cu Kα radiation (40 kV, 30 mA) and Ni filter plus a graphite monochromator. Thin films deposited at pH 3.8 for 4 h showed an XRD pattern of anatase-type TiO_2 having orientation similar to that of films deposited in the solution at pH 1.5 or 2.8 [10,36,37] (Fig. 5). The diffraction from parallel to c-plane such as (004) was observed as being strong compared to that of the randomly oriented powder diffraction pattern (Fig. 5). Pizem et al. [3] postulated that the commonly observed [00l] orientation of anatase films could be due to the slight polarity of the planes parallel to the [001] axis, unlike other low-index planes of this structure such as {100}, {110}, and {210}. The orientation and crystal growth mechanism are further discussed in a separate article [54].

Thin films were further evaluated by X-ray photoelectron spectroscopy (XPS; ESCA-3200, Shimazu Corporation, 1 × 10^−5 Pa). The X-ray source (Mg Kα, 1253.6 eV) was operated at 8 kV and 30 mA. The spectral peaks corresponding to Ti 2p (458.7 eV) were observed from thin films deposited on the silanol region (Fig. 6). This binding energy is higher than that of Ti metal (454.0 eV), TiC (454.6 eV), TiO (455.0 eV), TiN (455.7 eV) and Ti_2O_3 (456.7 eV), and similar to that of TiO_2 (458.4–458.7 eV) [31,55,56]. This suggests that the titanium atoms in thin films are positively charged relative to that of titanium metal by formation of direct bonds with oxygen. On the other hand, this spectrum was not observed from octadecyl group regions. The O 1s spectrum was observed from the silanol regions and divided into O 1s (530.2 eV) and O 1s (532.3 eV). O 1s (532.3 eV) can be assigned to the silicon oxide layer on the surface of the silicon wafer (532.0 eV [55]), whereas the binding energy of O 1s (530.2 eV) is similar to that of TiO_2 (529.9 eV [56], 530.1 eV [55]) as observed by Shin et al. [30]. This shows that oxygen is negatively charged compared with neutral oxygen molecules (531.0 eV), possibly through the formation of chemical bonds with Ti. The ratio of titanium to oxygen was estimated from the Ti 2p_3/2 (458.7 eV) spectrum and O 1s (530.2 eV) spectrum to be Ti/O = 1:2.0.

4. Conclusions

We proposed a novel method to fabricate nano/micro-scaled patterns of thin films and successfully fabricated patterns of anatase TiO_2 thin films in an aqueous solution at 50 °C. The difference in adhesive strength of thin films on substrates was employed for the site-selective elimination method. Heterogeneously nucleated TiO_2 and adhered homogeneously nucleated TiO_2 particles on OTS–SAM can be easily eliminated from the substrate by ultrasonication, whereas those on silanol groups maintained their adhesion during the immersion period. The essence of the site-selectivity of this method is a difference in adhesive strength. The site-selective elimination method can be applied to fabricate nano/micro-scaled patterns in the solution by the immersion of the substrate that has regions on which depositions adhere strongly and regions on which depositions adhere weakly enabling elimination by treatment such as ultrasonication.
Acknowledgements

This work was supported in part by the 21st Century COE Program ‘Nature-Guided Materials Processing’ of the Ministry of Education, Culture, Sports, Science and Technology. This work was partly supported by a Grant-in-Aid for Scientific Research (Grant-in-Aid for Young Scientists No 14703025, Exploratory Research No 14655239) from the Ministry of Education, Culture, Sports, Science and Technology granted to Y. Masuda.

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