Patterning titania with the conventional and modified micromolding in capillaries technique from sol–gel and dispersion solutions

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Abstract

We report TiO\textsubscript{2} patterns obtained by a soft-lithographic technique called ‘micromolding in capillaries’ using sol–gel and dispersion solutions. A comparison between patterning with a sol–gel and dispersion solutions has been performed. The patterns obtained from sol–gel solutions showed good adhesion to the substrate and uniform shapes, but large shrinkage, whereas those obtained from dispersion solution had high solid content, but exhibited poor adhesion and non-uniform shapes. A fabrication method of a layer-by-layer structured pattern is also demonstrated. This type of pattern may find application in sensors, waveguides and other photonics elements. The occurrence of an undesirable residue layer, which hinders the fabrication of isolated patterns, is highlighted and a method of prevention is suggested.

Keywords: micromolding in capillaries, soft lithography, patterning, TiO\textsubscript{2}, molding

1. Introduction

Titania (TiO\textsubscript{2}) is a metal oxide material with promising applications, as thick and thin films, in optics [1], dielectrics [2], photovoltaic cells [3], electrochromic displays [4], antireflection coatings [5], high-performance anodes in ionic batteries [6] and gas sensors [7–9]. It has a high refractive index (n\textsubscript{anatase} = 2.5) and good insulating properties, and therefore is widely used as a protective layer in very large scale integrated (VLSI) circuits. The high dielectric constant (\varepsilon\textsubscript{r} = 85 at 1 MHz) makes it an alternative to SiO\textsubscript{2} for ultrathin-gate-oxide dielectrics used in memory and logic devices [10].

The trend towards miniaturization of electronic and optical devices stimulates development of new and alternative fabrication techniques, and the so-called soft-lithographic techniques are the result of this trend [11]. These techniques are promising tools for the easy and low-cost fabrication of high-tech materials. Their most common feature is the use of a soft polymeric material, usually polydimethylsiloxane (PDMS) [11, 12], which can act both as a molding and stamping material. Micromolding in capillaries (MIMIC) is a promising molding technique [11–13]. Its basic principle is based on the formation of interconnected microchannels resulting from the conformal contact between the substrate and the mold. Therefore, the key feature is the formation of an interconnected network for the complete penetration of the solution via capillary force. The precursor solution can be a sol–gel, dispersion or some polymeric solution. However, the viscosity of the solution should be optimized for good filling versus high solids content of the final pattern.

Recently, several studies have been published on the soft-lithographic patterning of TiO\textsubscript{2}. Shi \textit{et al} [14] used the solvent-assisted soft-lithography (SASL) technique to pattern TiO\textsubscript{2} at submicrometer length scales. The dimensions (width and height) of the obtained patterns were controlled by...
parameters such as concentration of the solution, evaporation rate, time and temperature and not by the dimensions of the mold. Severe shrinkage associated with sol–gel-based materials has also been reported. Goh et al [15] applied embossing to produce a dense-array pattern from a thin layer of poly(methyl methacrylate) (PMMA) in combination with PDMS. In this way the good permeability and mechanical stability were combined. After use the mold was dissolved to avoid sticking to the substrate. So far, only two-dimensional (2D) patterns have been reported, i.e. patterns consisting of a single layer of TiO$_2$ on a flat substrate. Layer-by-layer type patterns, e.g. stacked woodpile structures of TiO$_2$ made by soft lithography have not yet been reported. Also the formation of a thin residue layer and its prevention have not been addressed.

In this work, we report on three important aspects of the MIMIC technique. Firstly, we have compared patterning with a sol–gel solution and a dispersion solution. Various physical factors such as degree of filling, adhesion to the substrate, shape evolution and shrinkage of patterns derived from both sol–gel and dispersion are the main parts of the discussion. Secondly, we have developed a method for the fabrication of layer-by-layer structured patterns. It allowed us to produce dual-layer woodpile patterns of TiO$_2$ using the MIMIC technique. The precursors utilized for this purpose were a sol–gel solution and dispersion, each with its own typical solids content. The third important aspect of this work concerns the formation of undesirable residue layers. We established a new technique based on chemical modification of the mold to prevent its occurrence.

2. Experimental details

Two types of TiO$_2$ solutions were prepared and utilized for patterning as explained in the following subsections.

2.1. Materials

Unless otherwise specified, reagents were used as received without further purification. Titanium(IV) isopropoxide (99.99%), 2-methoxyethanol (> 99.3%), polyethylene glycol (PEG) 600 (> 99%), acetylacetone (> 99%), polyacrylic acid (MW ∼ 1800) were purchased from Aldrich. TiO$_2$ powder (99%, anatase), ammonia (25% in H$_2$O), octadecyltrichlorosilane (OTS, > 95%) were purchased from Acros. Photocurable polyurethane (PU; NOA 73, viscosity 130 cps at 25°C) was purchased from Norland Products. Yttrium-stabilized zirconia (YSZ) grinding media was purchased from Inframat Advanced Materials. Polydimethylsiloxane (Sylgard 184) was provided by Dow Corning.

2.2. Sol–gel sol preparation

In a glove box, containing less than 0.5 ppm of water and oxygen, titanium(IV) isopropoxide was mixed with 2-methoxyethanol and stirred for 30 min at room temperature. Acetylacetone and PEG were added to this mixture and stirred for 2 h. The sol was then filtered with a 0.2-µm Teflon filter.

The viscosity of the solution amounted to about 2.99(7) mP s, as measured with a microviscometer (AmVn-HT, Anton Paar GmbH). The final titania sol had a Ti concentration of 0.6 M.

2.3. Dispersion solution preparation

We used commercially available anatase TiO$_2$ powder with 80 nm particle size. The powder was dispersed in distilled water containing a dispersant-stabilizing agent. The solution was then ball-milled for 72 h in YSZ grinding media with a particle size of 1.5 mm. Three solutions with solids loadings of 10, 20 and 30 vol.% were prepared.

2.4. Modification of PDMS mold

To avoid the formation of a residue layer in the MIMIC process, the PDMS molds were modified with the following procedure.

First, OTS was dissolved in toluene by stirring to make a homogenous solution. A 500 µl droplet of this solution was placed on a glass substrate and dried at room temperature and atmospheric pressure for 5–15 min.
Figure 2. SEM images of sol–gel-derived TiO$_2$ patterns produced with MIMIC: (a) pattern with two distinct areas, lines on the left and right have widths $w_l = 3$ and 5 $\mu$m, respectively; (b) line profile with $w_l = 3$ $\mu$m; (c) large-area pit pattern with $P_d = 800$ nm, showing some defects; (d) pit pattern having $P_d = 1.5$ $\mu$m; (e) surface contamination effect in line pattern with $w_l = 3$ $\mu$m and (f) effect of surface (S) to volume (V) ratio on the penetration length, lines on the left and right have $w_l = 800$ nm and 1.6 $\mu$m, respectively; (g, h) fork-shaped ends of penetrating sols, showing that the penetration rate of sols is faster in the corners of the channels: $w_l$ and $P_d$ are line width and pit diameter, respectively.

A pre-oxidized PDMS mold was placed in the thin as-dried OTS film, see figure 1(b). In this way only the protruding parts of the mold reacted with the siloxane reagent on the glass surface as shown in figure 1(c). After a certain reaction time (15–45 min) the mold was pulled away.

2.5. Substrate and mold preparation

A Si (100) wafer was cut with a diamond cutter into 1.5 $\times$ 1.5 cm$^2$ squares. A PDMS mold was cut into 1 $\times$ 1 cm$^2$ blocks and then blown with compressed air to remove dust and residual particles. The Si substrate was cleaned with a CO$_2$ snow jet and then with oxygen plasma for 5 min. The PDMS mold was then treated with oxygen plasma for 2 min to increase its surface energy (hydrophilicity) and hence its adhesion to the substrate. The water contact angles of both the substrate and PDMS after oxygen plasma treatment were below $5^\circ$.

2.6. Analysis

Structural characterization was performed with x-ray diffraction (XRD). Surface analysis was carried out with a scanning electron microscope (SEM) operated at a voltage between 0.5 and 30 keV (JEOL, Tokyo). Atomic force microscopy (AFM) imaging was performed in tapping mode.
on a Nanoscope IV instrument (Veeco, Digital Instruments, Santa Barbara, USA).

3. Results and discussion

3.1. Patterning of TiO$_2$ with micromolding in capillaries

3.1.1. Patterning of sol–gel-derived TiO$_2$. The plasma-treated mold was gently placed on the Si substrate. This mold contained two sets of lines of 3 and 5 µm width ($w_l$), spaced by 6 and 10 µm, respectively, whereas the height was 1 µm. A drop of 10–50 µl of the sol was poured at the entrance of the capillaries. After complete filling of the channels of the mold via capillary action, the wet pattern along with the mold was placed on a hot plate heated to 40 °C for 10–15 min until complete evaporation of the solvent into PDMS. The mold was peeled off carefully without deformation of the patterned lines. The sample was further heated to 80 °C for 30 min and finally annealed at 550 °C for 60 min.

Figure 2(a) shows sol–gel-derived TiO$_2$ lines obtained with MIMIC. The cross-sectional profile of the lines is somewhat triangular in shape after thermal processing, as can be seen in figure 2(b). This shape is probably the result of shrinkage of the pattern upon drying. However, in contrast to other materials such as Pb(Zr$_x$Ti$_{1-x}$)O$_3$, no gel formation occurred, and therefore no double-peak profile evolved. Other factors such as viscosity, types of solvents, pH and precursor size may also affect the final shape of patterns. Nevertheless, the drying behavior is believed to be the most important factor. For 2D micropatterns, the cross-sectional shape is often less important than its lateral structure. However, rectangular shapes with straight angles between faces are needed for some applications, e.g. in stacked woodpile structures. Thus, it is important to either modify the technique or use some alternative technique that circumvents this problem.

One of the key requirements in MIMIC is that the features to be patterned should be interconnected to allow the solution to penetrate all voids between the mold and the substrate. A mold with two distinct areas of pillars of diameter ($P_d$) 800 and 1500 nm, respectively, was applied to make pit-patterned films. Figures 2(c) and (d) show such pit-patterned films of titania with $P_d$ of 800 and 1500 nm, respectively. The small defects and discontinuities, which occur quite regularly, can be attributed to dust particles on Si or PDMS, or they may have resulted from the peel-off process of the mold. In the fabrication of micromolded component devices, the effect of contaminants and dust particles becomes more important as the feature sizes get smaller. After treating the substrate and PDMS mold with oxygen plasma their surface energy becomes higher. After treating the substrate and PDMS mold with oxygen plasma their surface energy becomes higher. After treating the substrate and PDMS mold with oxygen plasma their surface energy becomes higher. After treating the substrate and PDMS mold with oxygen plasma their surface energy becomes higher.

Figure 2(e) shows the effect of a local contamination with low surface energy on the advancing of the liquid during filling of the channels. The surface energy of the contaminant is lower than that of the penetrating solution, so that the solution cannot wet the contaminated area, and the patterning process is discontinued in every channel that contains the contaminant.

During the MIMIC process, filling of the channels and drying of the solution take place simultaneously. Kim et al [17, 18] have derived a thermodynamic model to describe the filling of a capillary under the influence of capillary force. Using this equation the rate of liquid flow can be estimated from its surface tension, viscosity, cross-sectional area and length of the penetrating capillary:

$$\frac{dz}{dt} = \frac{r_H \gamma_{LV} \cos \theta}{4 \eta z} = \frac{r_H (\gamma_{SV} - \gamma_{SL})}{4 \eta z}.$$  (1)

Here $r_H$ is the hydraulic radius (ratio of volume to surface area), $\gamma_{SV}$ and $\gamma_{SL}$ are the solid–vapor and solid–liquid surface tensions, respectively. $\eta$ is the viscosity of the liquid, $z$ is the filled length of the channel, and $t$ is time.

Although equation (1) is derived for a tubular capillary, it provides good estimates for other shapes as well. According to this equation, penetration should proceed indefinitely. In practice, however, the process stops after a certain time and/or length of penetration. This is due to the fact that as the solution penetrates into the channel, solvent from the solution diffuses into the microporous PDMS walls, so that the solids content in the entering solution increases continuously, in particular near the capillary front. As a result, the viscosity of the solution increases, reducing the penetration rate. Ultimately, the viscosity becomes so high that it prevents further penetration. Figure 2(f) shows the effect of surface tension on volume ratio of lines with different dimensions on the ultimate penetration length of the patterned lines. The lines with smaller diameter, i.e. high surface to volume ratio dried faster than the wider ones. As a result, the penetration length was shorter for narrow than wide channels.
Figure 4. Sol–gel-based TiO$_2$ patterns obtained with MIMIC, showing cracks due to shrinkage after thermal processing of (a, b) line patterns and (c, d) pit patterns.

Heule et al [19] reported on the patterning of powder-based tin oxide (SnO$_2$) patterns by MIMIC. The formation of fork-shaped spikes was attributed to the faster penetration of the solution in the corners of the channels. We observed the same phenomenon while patterning sol–gel-based TiO$_2$ lines. However, it only occurred when the mold was left on the substrate for prolonged periods of time, i.e. 60 min or more. Examples are shown in figures 2(g) and (h). Another possible reason could be the lack of supply of solution to further fill the capillaries. Incomplete filling could thus lead to the formation of these spikes.

3.1.2. Structural analysis. The diffraction pattern of a sol–gel-derived TiO$_2$ patterned film on a Si (100) substrate is shown in figure 3. All peaks correspond to the anatase phase of TiO$_2$ and to the Si (100) substrate. The film was initially dried at 40°C for 10 min and then at 80°C for 30 min. Subsequently it was annealed at 550°C using a heating and cooling rate of 5°C min$^{-1}$ and a holding time of 60 min.

3.1.3. Topographic study of patterns—shrinkage and cracking. The MIMIC technique requires solutions with a low viscosity for fast and complete penetration throughout the entire network of channels. To ensure a sufficiently low viscosity, the solids content should remain low. Depending on the material, this results in huge volumetric shrinkage of the patterns during drying and thermal annealing [16, 20]. This reduces the fidelity of the resulting patterns. Furthermore, some sort of functionalization of the patterned surface is required for most applications, such as deposition of top electrodes onto a pre-patterned film. Therefore, such patterns should have a rectangular shape. As discussed above, shrinkage reduces the control over the final shape in MIMIC processes.

Another important aspect is crack generation in patterned films. Films that are heated and then cooled to room temperature experience compressive and/or tensile stresses. These intrinsic stresses normally originate from one or more of the following reasons: (a) volumetric shrinkage upon thermal annealing, (b) differences in coefficients of thermal expansion between the substrate and film, (c) phase transformations or (d) clamping of the film to the substrate. Intrinsic stresses can ultimately result in the cracking of thin films and patterns.

Cracking has two major stages: crack initiation and crack propagation. It is interesting to note that the tendency to cracking was considerably lower in MIMIC-patterned films than in spin-coated thin films. This is because cracks can propagate in all direction in thin films to release internal stresses. However, in patterned lines or similar structures with micrometer-scale lateral dimensions in at least one direction, developed stresses can relax in the direction that is perpendicular to both the plane of substrate and the main axis of the line. In other words, since all patterned features (lines and pillars) are isolated from each other, a crack that is initiated in one feature cannot propagate to another one, provided that the patterned features are not connected via a thick residue layer. Cracks are formed mostly as the result of in-plane tensile stresses that occur in the direction of the lines. The crack planes are therefore oriented perpendicular to this direction.

Figures 4(a) and (b) show examples of shrinkage and cracking phenomena of multiple and single TiO$_2$ lines. The
cracks in a line do not propagate through the entire pattern, but mostly run perpendicular to the direction of the line. Similarly, figures 4(c) and (d) show the effects of shrinkage of pit-patterned films. However, in this case the predominant shrinkage takes place in the vertical rather than lateral direction [16, 20]. This is because the patterned film is clamped to the substrate in the lateral directions and is free to move vertically. For these TiO$_2$ patterns, the total volumetric shrinkage is 97%.

3.1.4. Dispersion-derived TiO$_2$ patterns. To avoid severe shrinkage and obtain denser and more regularly shaped patterns, MIMIC was also applied to dispersion-based TiO$_2$ with solids contents of 10, 20 and 30 vol.%. The best-quality pattern was observed for the 10 vol.% samples. Dispersions with higher solids contents showed a poorer quality of channel filling, because their higher viscosities hampered easy penetration into the channels. The dispersions were prepared as described in section 2.3. Figures 5(a) and (b) show SEM images of TiO$_2$ line patterns with a line width of 3 µm derived from 10 vol.% dispersions. Figure 5(c) shows an AFM topographic image of this line pattern. The cross-sectional profile of the lines derived from dispersions was more rectangular compared to sol–gel-derived lines, although they were not completely rectangular either. Furthermore, the solids mass per unit surface area in the final patterns was higher for the former lines. The dispersions with higher solids contents showed a decreased penetration rate and length because of their high viscosity. The filling rate also decreased because of the continuous drying of dispersions during the MIMIC process. These observations agree with the results of Heule et al [19], although those authors used molds with semi-circular channels.

Figures 5(d) and (e) show SEM images of a pit-patterned film with $P_d \approx 3 \mu m$ after thermal treatment. Figure 5(f) shows an AFM scan of a pit with $P_d \approx 1.5 \mu m$. Some coarse grains/particles were observed at the edge of the pits. We noticed three drawbacks in dispersion-based solutions. Firstly,
the adhesion of the patterns to the silicon substrate was poor in comparison with sol–gel-derived films. Secondly, the patterns were much more porous and needed higher sintering temperatures (about $800^\circ C$ or higher) for densification. High processing temperatures restrict the choice of substrate material. Thirdly, the surface roughness of patterns derived from dispersions was also higher, because the agglomeration in solution resulted in larger and coarser particles.

3.2. Layer-by-layer patterning of TiO$_2$ from dispersion solutions

As discussed in the introduction, these patterns may find application in photonics as waveguides and photonic crystals. Kim et al [21, 22] applied UV embossing technique for the fabrication of a multimode optical waveguide derived from an organic–inorganic hybrid material. Later the same group made use of nanoimprint lithographic method for the fabrication of sub-50-nm nanostructures of hybrid materials having a high refractive index [23, 24].

In this work, titania dispersions were used to stack two layers of TiO$_2$ lines by applying MIMIC. Figure 6(a) depicts the procedure adopted for patterning these structures. The first layer was patterned with conventional MIMIC as described in section 3.1. The pattern was dried at 80$^\circ C$ for 1 h. Then, a thin film of polyurethane (PU) was spin-coated on top at
SEM images of TiO$_2$ line patterns prepared by MIMIC using a non-silanized, plasma-treated mold (a), and a mold that was silanized after 2.5 min (b) or 5 min (c) of oxygen plasma treatment.

To improve the adhesion between the substrate and mold, their surface energies were increased by oxygen plasma treatment [25–28]. It leads to a measurable decrease of the water contact angle, and therefore to an increase of the capillary force on the penetrating solution. This will increase the penetration rate and final penetration length when all other variables remain the same. The surfaces of the substrate and mold are not perfectly flat. On the nanoscopic level they show irregularities, which may prevent confocal contact in some local areas, leading to the formation of very small pores between the substrate and mold (figure 7a). According to equation (1), the penetration rate (dZ/dt) is proportional to the radius of the capillary. This implies that the narrower the channel, the larger will be the capillary force that it exerts. Thus, the capillary force exerted by the very small pores between the substrate and mold is much larger than the capillary force exerted by the micrometer-sized capillaries and channels. This inevitably leads to the formation of an unwanted thin layer underneath the mold, which is called a ‘residue layer’. Theoretically, a residue layer may form when the size of the precursor entities in solution is smaller than the size of the smallest pores. The thickness of the residue layer is typically between 5 and 50 nm. On the other hand, if the surface energies of the substrate and mold are not increased, the contact angle of the precursor solution inside the channels is unfavorable. This prevents the formation of a residue layer, reduces the penetration length of the liquid, and leads to incomplete filling of the mold. Alternative measures should be taken to achieve sufficient penetration without formation of a residue layer.

When MIMIC is being used, an ideal configuration would be to have hydrophilic micro-capillaries and a mold with a comparatively hydrophobic interface in areas where it contacts the substrate. This is schematically shown in figure 7(b). To fabricate such a mold, we adopted the experimental procedure described in section 2.4.

Figure 8 shows SEM images of TiO$_2$ lines made by MIMIC. As can be seen in figure 8(a) the use of a chemically unmodified plasma-treated mold led to the formation of a residue layer between the lines. Figure 8(b) shows the effect of modifying the mold with OTS. The residue layer was reduced to a large extent and only traces of residue layer could be observed. In this case the mold had been treated with oxygen plasma for 2.5 min prior to silane layer deposition. Even better results were obtained when the mold was plasma-treated for 5 min prior to silanization, as shown in figure 8(c). No residue layer was observed at any location. The quality and reproducibility of lines that can be made with these molds depends on many factors, which are explained below.

3.3.1. Oxygen plasma treatment. The duration of oxygen plasma treatment, which used to increase the surface energy of the PDMS mold prior to silanization, is of prime importance. Molds that had been plasma-treated for too long became so hydrophilic that the OTS diffused to the inner walls of the channels, making them hydrophobic. On the other hand, when the molds were plasma-treated for a very short period of time (<2 min), incomplete filling of the capillary channels
occurred during the patterning step. We found that an oxygen plasma treatment for 5 min yielded water contact angles smaller than 3°. This period of treatment was sufficient, as very thin or no residue layers were observed in combination with complete filling of capillaries.

3.3.2. Concentration of silane. Another important factor is the concentration of OTS in the solvent. The optimum concentration of OTS in toluene in this experiment was found to be $2.02 \times 10^{-5}$ M. Concentrations below this value resulted in the formation of a non-uniform residue layer, whereas higher concentrations reduced the penetration length. This is because high OTS concentration makes the channels of the mold hydrophobic through diffusion, and thus reduces the penetration length during the MIMIC process.

3.3.3. Time of contact between mold and silane. The time of contact of the oxidized mold with the silanized glass substrate is also of importance. Very long contact times resulted in diffusion of organosilane to the capillaries, making them more hydrophobic and increasing the contact angle, thereby reducing the capillary force. Short contact times resulted in some residue layer, because poor-quality or an incomplete OTS layer was formed. Contact times of 5–45 min were applied in our experiments with the best results achieved for 15 min duration.

In summary, modification of the protruding parts of the mold allowed to avoid residual layer formation. The balance between capillary filling and residue layer formation can be established by optimizing the oxygen plasma treatment, the amount and concentration of organosilane and the time of contact between mold and silane.

4. Conclusions

Micromolding in capillaries was successfully used to form dual-layer TiO$_2$ patterns on Si substrates. Two types of liquids, namely sol–gel solution and dispersion were used as precursors, and both were found to have their own advantages and limitations. The sol–gel-derived patterns were much denser and showed good adhesion to the substrate. However, the large shrinkage and non-uniform shape after drying and thermal annealing limits their use in layer-by-layer pattern fabrication. In contrast, patterns derived from dispersions showed less or no shrinkage and their shapes changed less compared to the sol–gel-derived patterns. Nevertheless, their adhesion to the substrate was poor. They were also more porous and needed higher sintering temperatures for full densification. This limits their use to pattern substrates that are not stable at high temperatures.

Another important aspect of the MIMIC technique is the formation of a residue layer between molded features, which can be avoided by chemical modification of the protruding features of the PDMS mold.

We believe that MIMIC has a strong potential for the fabrication of a variety of materials from chemical solutions with little or small variations in their respective process parameters. The produced 2D patterns may find application in gas sensors, where large surface area is needed. The layer-by-layer woodpile patterns can be useful in photonics, e.g. as waveguides and photonic crystals.

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