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Effect of the film thickness on the fabrication of ordered TiO_2 thin film microstructures by transfer printing

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Abstract

This paper describes a transfer printing technique for directly patterning ordered TiO_2 thin films onto Si substrates. Two- or three-dimensional TiO_2 structures can be fabricated onto an Si substrate depending on the coating film thickness, which is controlled via the liquid phase deposition process parameters and attractive interaction forces between a poly(dimethylsiloxane) stamp and a polyelectrolyte layer during the transfer printing process. This additive transfer process is mediated by the presence of a thiol (–SH)-terminated 3-mercaptopropyltrimethoxysilane self-assembled monolayer on the wafer surface. The transferred patterns are chemically bonded to the wafer surface, exhibiting strong adhesion. The attractive interaction forces between the stamp and the polyelectrolyte layer was weak enough to allow ready detachment of the patterns from the stamp during printing. Even the parts of a continuous TiO_2 film that are not in contact with the substrate effectively transfer to form a free-standing structure. With long and short deposition times, three-dimensional structures and ordered two-dimensional round-hole grid structures, respectively, are obtained after the removal of the stamps.

Keywords: Transfer printing; Self-assembled monolayer; TiO_2 microstructures

1. Introduction

The stamping technique known as nanotransfer printing (nTP) [1,2] is operationally simpler and less expensive for high-resolution patterning over large areas compared to conventional photolithography patterning. During nTP, interfacial chemical reactions occur when the stamp and substrate are brought into contact. Surface chemical bonding interactions between the substrate and the thin solid layers of "inks" enable efficient transfer from the stamp to the substrate by contact printing. As first reported in the literature, nTP is based on the adhesive transfer of a patterned metal [1–7] thin film from a stamp to various substrates [8,9] with tailored surface chemistry. The process has four key steps, namely the fabrication of a patterned stamp, coating of a continuous metal thin film, contact with a substrate surface, and removal of the stamp from the substrate. Coating a stamp with a collimated flux of ink generates a discontinuous film on raised and recessed regions. Placing this ink-coated stamp onto a flat, smooth substrate leads to wetting, which provides intimate contact between the two surfaces without the need to apply external pressure. Mild heating (~50–80 °C) for a sufficient duration followed by the removal of the stamp leaves the ink pattern in the geometry of the relief features on the substrate. Established methods for nanofabrication, such as scanning probe techniques, deep ultraviolet (UV) projection mode photolithography, and electron beam lithography, are well suited for building two-dimensional structures on flat surfaces. A number of techniques based on stamping [10,11], embossing [12], and printing [13] have been developed for patterning nanoscale structures that can be useful for applications in photonics, microelectromechanical systems, and electronics. These techniques not only provide similar patterning capabilities with simple,

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low-cost tools and avoid many limitations of conventional methods, but also generate certain types of three-dimensional structures. In recent years, the controlling the position, diameter, or morphology of metal nanostructures has been reported widely. However, the micro- or nanostructures of metal oxide have not been reported to be fabricated via the transfer printing. A major challenge for researchers has been to find ways to overcome the crack due to the brittle properties of metal oxide. The present study uses a recently developed contact printing technique that combines the transfer printing process and low-temperature liquid phase deposition (LPD) [14] to build two- and three-dimensional TiO_2 thin films depending on the coating film thickness. The film thickness is controlled via the LPD process parameters and the attractive interaction forces between a poly(dimethylsiloxane) (PDMS) stamp and a polyelectrolyte layer. This approach is expected to be able to produce much more complex structures.

2. Experimental procedures

Poly(diallyldimethyammonium chloride) (PDAC, $(C_8H_{16}ClN)_n$, Mw ~ 20 k, Aldrich), poly(sodium 4-styrenesulfonate) (PSS, $(C_8H_7NaO_3S)_n$, MW ~ 70 k, Aldrich), poly(allylamine hydrochloride) (PAH, $(C_3H_8ClN)_n$, FW ~ 93.56, Aldrich), and 3-mercaptopropyltrimethoxysilane (MPTMS, $C_6H_{16}O_3SSi$, Fluka, 97%) were used as received. PDMS ($CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$, Sylgard 184) was purchased from Dow Corning. The Si substrates used in this work were initially treated with a chemical cleaning process to remove contaminants [15]. The Si substrates were cleaned in piranha solution (H_2SO_4:H_2O_2 = 4:1) and rinsed using deionized water. A 20 nm-thick Au thin film was evaporated onto the substrate surface. Immediately after Au deposition, the substrate was placed in a 10 mM MPTMS solution for 5 min, washed with methanol solution, and then dried under a stream of nitrogen. The PDMS stamp was fabricated by thermal curing a mixture of PDMS resin and a curing agent at 60 °C for 1 h. The PDMS stamp was then separated from the master stamp [16]. The surface modification of PDMS was carried out by polyelectrolyte multilayers (PEMs), which were fabricated by alternately exposing a surface to cationic and anionic polyelectrolytes in solution [17]. TiO_2 was deposited onto the modified PDMS stamp by LPD. The LPD TiO_2 films were prepared as follows: ammonium hexafluorotitanate, $(NH_4)_2TiF_6$ (ACS reagent grade, Aldrich), and boric acid, H_3BO_3 (ACS reagent grade, Aldrich), were separately dissolved in water to give concentrations of 0.05 M and 0.15 M, respectively. These two solutions were then mixed together at 30 °C and used as the reaction solution [18]. After the LPD process, the PDMS stamps were air-dried. A TiO_2-coated PDMS stamp with relief features in the desired geometry was brought into contact with the treated substrate at 60 °C for 5 min. The elasticity and the mechanical conformability of the PDMS stamp ensure atomic-scale contact at the stamp/substrate interface without the need to apply pressure. Removing the stamp from the substrate completes the pattern transfer process. The UV–visible absorption spectrum was obtained using a UV–visible spectrometer (UV-2001, Hitachi, Japan). The pattern geometry, height, and shape were measured using a scanning electron microscope (SEM; S-3000N, Hitachi, Japan)

3. Results and discussion

The surface hydrophilicity of the stamp is known to strongly influence the adhesion or deposition of a material. To hydrophilize the PDMS stamp, a hydrophilic self-assembled monolayer (SAM) was formed on it via the layer-by-layer process. Fig. 1(a) and (b) shows top-view and low-magnification SEM images of the hydrophilized PDMS stamp, respectively. The inset shows a cross-sectional view. The round-hole stamps of PDMS, with a feature size of approximately 10 μm with 20 μm spacing, were stamped by curing Sylgard 184 PDMS against a master. The depth of the relief structure was confirmed to be 3 μm by the tilted SEM images of the PDMS stamp shown in the inset of Fig. 1(a). The surface of the PDMS stamp was modified by immersing the stamp into an aqueous solution of PAH to allow the adsorption of a polycation layer onto the surface. Alternating adsorption from PSS and PDAC solutions yielded a complete polyelectrolyte multilayer on the stamp surface, which is denoted as $PAH(PSS/PDAC)_n$. The final polyelectrolyte was PDAC, resulting in a positively charged top multilayer thin film. The hydrophobic interactions between the PAH base layer and the PDMS surface must be weaker than the electrostatic interactions between the PDAC top surface and the negatively charged substrate onto which the film is transferred [19]. The effect of the number of (PSS/PDAC) bilayers on the wetting behavior of the stamp was measured from the contact angle of water droplets. With more than three (PSS/PDAC) bilayers, i.e., $n > 3$, the surface of the PDMS was fully covered with the polyelectrolyte multilayer, making it hydrophilic [17]. The UV–visible spectra of the PSS/PDAC films on PDMS were used to identify the PSS assembled onto the surface of the PDMS stamp. Fig. 1(c) shows the absorbance of PSS at λ_{max} (232 nm) versus the number of bilayers. The absorption peak at around 232 nm is attributed to the phenyl group in PSS, possibly transferring from $\pi \rightarrow \pi^*$. The linear increase of the absorbance with the number of layers indicates a continuous deposition process due to the electrostatic interaction [20,21]. This indicates that the PSS molecules assembled onto the surface of the PDMS stamp.

In the LPD process, TiO_2 film is directly deposited onto the modified surface of the PDMS stamp according to the following chemical reaction:

$$TiF_6^{2-} + 2H_2O \Leftrightarrow TiO_2 + 6F^- + 4H^+ \quad (1)$$

$$H_3BO_3 + 4H^+ + 4F^- \Leftrightarrow HBF_4 + 3H_2O \quad (2)$$

Metal oxide thin films are formed via a hydrolysis equilibrium reaction of metal-fluoro complex ions and an

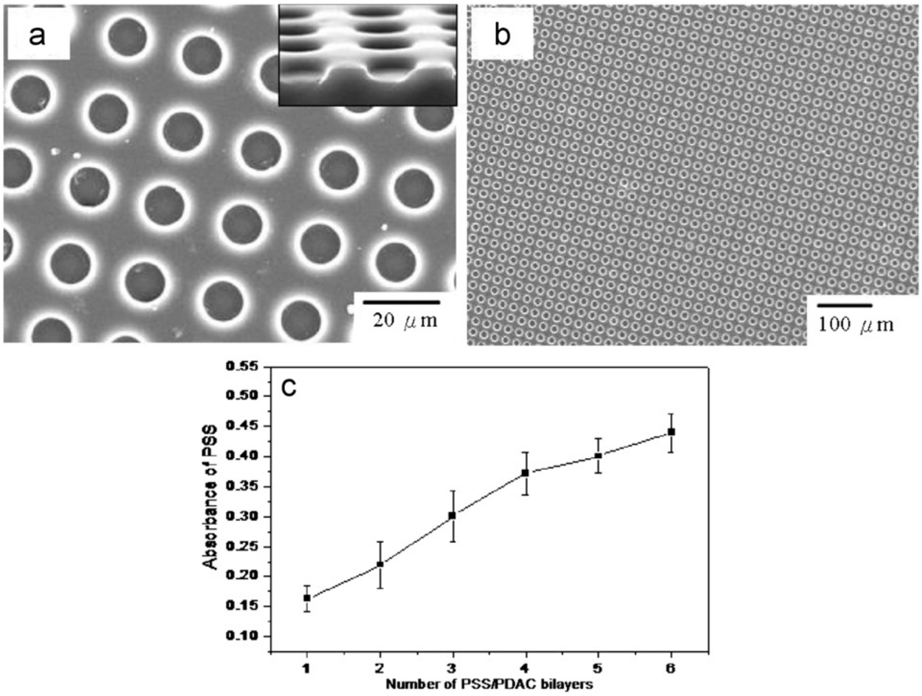

Fig. 1. (a) Top-view and (d) low-magnification SEM images of hydrophilized PDMS stamp. (c) Absorbance of PSS at $\lambda_{\max}$ (232 nm) versus the number of bilayers. The inset of (a) shows a cross-sectional view.

F^--consuming reaction of boric acid, which acts as a scavenger for F^- [22]. The hydrolysis reaction of metal-fluoro complex ions $\left(\mathrm{TiF}_6^{2-}\right)$ in the treatment solution for deposition follows equilibrium reaction (1), with the right-hand side shifted by the addition of boric acid, which readily reacts with the F^- ions to form stable complex ions (Eq. (2)). In general, the chemical reaction speed depends on the reaction temperature, concentration, and pH value. The coating film thickness on the PDMS stamp was estimated from the change in the coating film thickness as a function of reaction time. Fig. 2 shows the effect of reaction time on the coating film thickness for reaction temperatures of 30 °C, 40 °C, and 50 °C. The pH value of the reaction solution was adjusted to 3.7 in all cases. The deposition yields for TiO_2 increase with increasing reaction temperature. The deposition rate for the reaction temperatures of 30 °C and 40 °C increased with reaction time up to 4 h, was constant to 8 h, and then decreased gradually. At the initial stage of the deposition rate increasing with time, individual nuclei formed on the stamp and the number of nucleation sites increased with reaction time. At the stage of a constant rate, the nuclei grew with reaction time. Finally, the decrease in the deposition rate is likely due to the decrease in the reactant content. When the reaction time was 4 h at a reaction temperature of 50 °C, the saturated coating film thickness reached approximately 50 nm, smaller than those for the other reaction temperatures. During the solution reaction, nucleation and growth occur either in solution (homogenous nucleation) or on the surfaces of the introduced solid phase (heterogeneous nucleation). Successful film formation relies on the promotion of heterogeneous nucleation. Solubility generally depends on the solution pH and the concentration of the species in solution. As the solution crosses over from a solvated state to a state of supersaturation, film formation can occur. It is vital to assure that the state of supersaturation is one that promotes film growth and not homogeneous nucleation and precipitation [23,24]. Another important factor in the LPD process is interfacial energy. When a substrate whose interfacial energy is lower than that of a growing homogeneous nucleus is introduced into a growth solution, heterogeneous growth is

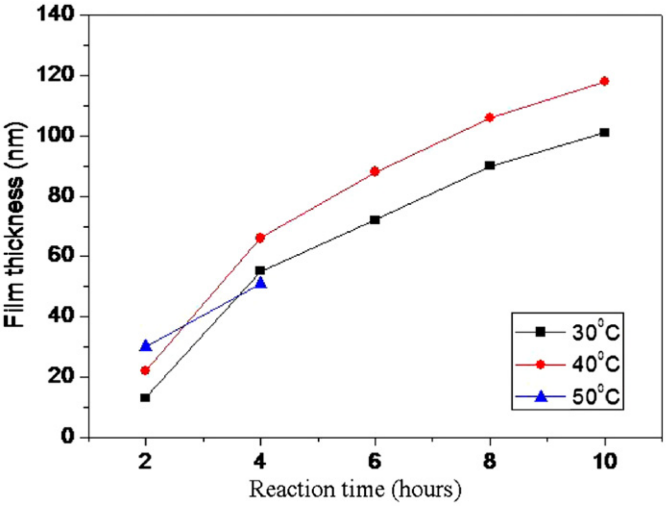

Fig. 2. Effect of reaction time on coating film thickness for reaction temperatures of 30 °C, 40 °C, and 50 °C. The pH value of the reaction solution was adjusted to 3.7 in all cases.

favored. Hence, heterogeneous growth on a seeded substrate occurs at lower levels of supersaturation than nucleation and growth in homogeneous solution.

During the initial stage of the deposition, the interaction of the TiO_2 nanoparticles with the SAM surface competes with the colloidal interactions between the initially formed TiO_2 particles. The uniform TiO_2 deposition coverage on the substrate at the initial stage leads to the growth of smooth films at a reduced deposition rate, suggesting that the film growth rate and the extent of homogeneous precipitation are dependent on the interaction of the substrate with the deposition solution [25]. An 80 nm-thick TiO_2-coated PDMS stamp (7 h reaction time) with relief features in the desired geometry was brought into contact with the treated Si substrate at 60 °C for 5 min. The top and side views of the three-dimensional structural TiO_2 thin film produced by transfer printing after peel-off are shown in Fig. 3(a) and (b), respectively. The attractive interaction forces between the stamp and the polyelectrolyte layer was weak enough to allow ready detachment of the patterns from the stamp during printing. Even the parts of a continuous TiO_2 film that are not in contact with the substrate effectively transfer to form free-standing structures. With a 5 h reaction time, the TiO_2 could not transfer a uniform structure, which is due to the weak cohesion forces of TiO_2 thin films at the edge of the stamp, as shown in Fig. 3(c). The arrow indicates a region where no pattern was transferred. The PDMS stamps were densely covered with a thin uniform TiO_2 layer for a reaction temperature of 30 °C after 3 h of LPD deposition. In this case, a 50 nm-thick TiO_2-coated elastomeric PDMS stamp with appropriate relief features was brought into contact with the treated substrate. After the removal of the stamp from the substrate, the brittle TiO_2 film on the sidewall of the stamp tended to fracture, and cracks occurred at the edge of each column due to stress concentration. A two-dimensional TiO_2 structure was fabricated on the substrate, as shown in Fig. 4(a). Fig. 4(b) shows an angled view that illustrates the curved edges on the holes. The depth of the relief structure was confirmed to be the thickness of the TiO_2 thin films deposited on the stamp. A schematic representation of the two types of structure and the related formation mechanism are shown in Fig. 5. There are four steps in the printing process: (a) PDMS replication, (b) surface modification of PDMS stamp using SAM treatment, (c) material deposition on the modified PDMS stamp by LPD, and (d) printing and detachment of PDMS stamp. The initial hydrophobic weak polyelectrolyte, PAH, in conditioning the hydrophobic, untreated PDMS stamp is critical to the nanotransfer printing process. The first layer creates a charged, wettable surface via non-electrostatic interactions for the construction of a multilayer, $(PSS/PDDA)_n$. The Si substrates used in this work initially had a thin film of Au deposited on the surface. The substrates were then placed in MPTMS solution. The thiol-terminated MPTMS SAM bonds strongly to gold. Furthermore, the thiol groups can be easily oxidized into sulfonic acid groups ($–SO_3H$) [17,26], which can provide both a high degree of surface acidity and net negative charge to bond with TiO_2 thin films. During the printing transfer process, for long and short deposition times, three-dimensional structures and ordered

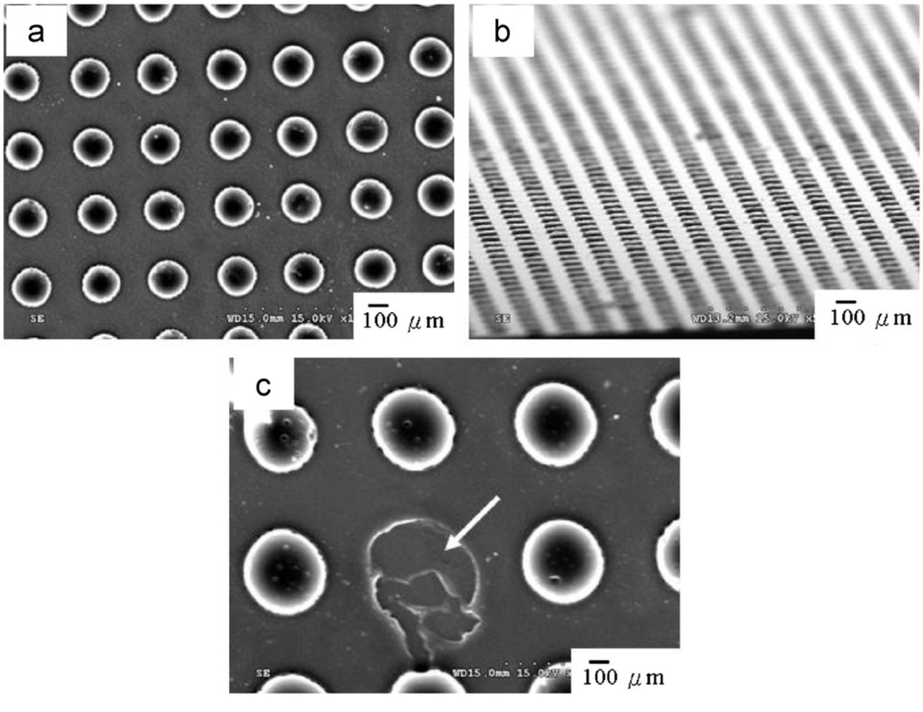

Fig. 3. SEM images of three-dimensional TiO_2 patterned thin films produced by transfer printing.

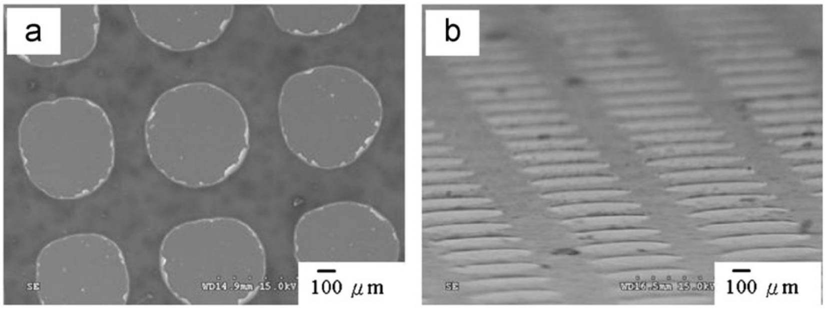

Fig. 4. SEM images of two-dimensional TiO_2 patterned thin films produced by transfer printing.

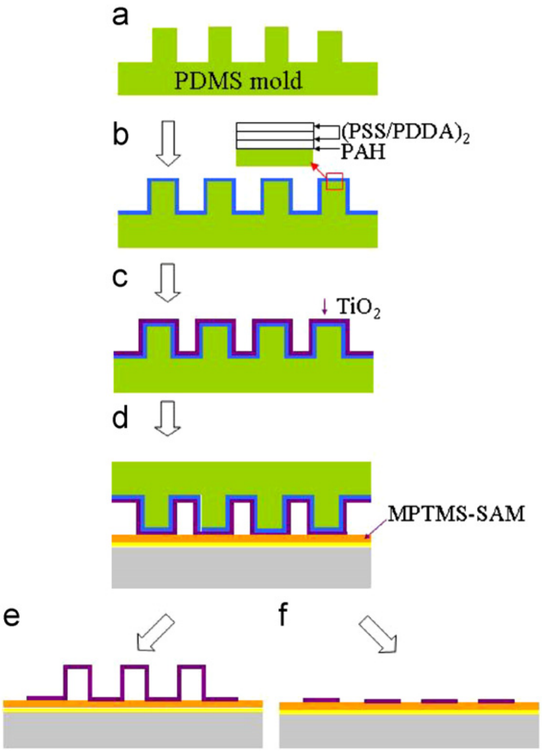

Fig. 5. Four steps for nanotransfer printing: (a) PDMS replication; (b) surface modification of PDMS stamp using SAM treatment; (c) material deposition onto modified PDMS stamp by LPD; (d) printing and detachment of PDMS stamp. (e) Three- and (f) two-dimensional structures.

two-dimensional round-hole grid structures, respectively, are obtained after the removal of the stamps, as shown in Fig. 5(e) and (f).

4. Conclusion

In summary, multilayer films were prepared on a PDMS stamp and Si substrate using a self-assembling method. The surface chemistry, thin film deposition, and thin film thickness on the stamp are important for this method. We also have developed a method combining transfer printing and LPD processes to fabricate two- or three-dimensional structures. The thickness was determined for patterning two- or three-dimensional structures, 50- or 80 nm-thick TiO_2-coated PDMS stamp, with a low density of defects and minimal distortion. In addition, the technique can be extended to multi-component structures through multiple sequential transfer steps utilizing films with various functionalities to create complete devices or device components in a simple fabrication process. The transfer can be made directly to glass, plasma-treated plastics, and other metal oxides. Structural thin films with electronic, biomedical, electrochemical, optical, and sensor functionalities can be integrated directly into devices using this approach.

Acknowledgments

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