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Transfer Printing Water-Soluble Inorganic Salts**

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This paper reports the first example of the fabrication of KNO_3, K_2CO_3, $CuSO_4$, NaOH, and mixed-inorganic-salt (KNO_3 and KOH) patterns using a transfer-printing (TP) technique. The transfer quality is found to be related to the concentration of the salt solutions. By varying the immersion time, it is possible to control the heights of the raised features of the transfer-printed salts from the nanoscale to the submicrometer scale. Utilizing these inorganic salts as water-soluble masks for microfabrication is demonstrated using patterned NaOH films. The use of water as a developer solvent demonstrates the potential utility of the patterning of inorganic salts as a low-cost, simple, and, more importantly, environmentally friendly route towards accurate patterning of different materials.

1. Introduction

Crystalline inorganic structures of microscale dimensions play an important role in microelectronics, optics, information storage, biomedical implants, catalysis, and separation technologies.[1–5] Patterns of crystalline inorganic semiconductors are typically fabricated using (photo)lithographic techniques in combination with etching.[6–10] Recently, the bottom–up growth and assembly of inorganic crystals[11–14] of biological relevance have also received considerable attention. These methods have produced an impressive array of patterned inorganic media, but most of them require multistep patterning procedures to produce etch masks or templates for structuring the inorganic material. Recent progress in micro- and nanotechnology depends greatly upon design and development of novel, simple, and reproducible patterning strategies to fabricate structures in a great variety of materials like polymers, metals, and semiconductors. A set of soft-lithographic techniques[15] (microcontact printing, replica molding, microtransfer molding, micromolding in capillaries, and nanotransfer printing[16]), which has been proven to be very powerful for patterning a range of materials at the micro- or nanoscale with relatively low cost and high efficiency, has been developed in the past decade. Transfer printing (TP) has emerged as a versatile soft-lithographic method to deposit a range of inorganic materials[17–21] and polymers[22–24] onto solid substrates with submicrometer resolution. In this paper, we present the first example of directly patterning planar substrates at the (sub)micrometer scale with inorganic salts by TP. The patterned inorganic salts were utilized as water-soluble masks for further microfabrication. Current efforts on the development of water-soluble masks/templates are aimed at the use of new water-castable polymeric materials,[25–31] while in this paper we present the largely unexplored use of simple, widely available, inorganic salts as masks.

2. Results and Discussion

The procedure for TP of salts is schematically shown in Figure 1: firstly, a poly(dimethylsiloxane) (PDMS) stamp with a 4 μm period pattern was briefly O_2-plasma oxidized to render its surface hydrophilic; the hydrophilic PDMS stamp was then immersed in a concentrated salt solution (in a typical example, a 0.2 M $CuSO_4$ solution in water) at 55 °C for 1–4 h, resulting in a thin salt layer depositing on the PDMS surface. Finally, the stamp was dried with N_2 gas and placed onto a Si/SiO_2 substrate wafer for 10 min. The stamp wetted the surface without any additional pressure. In those experiments where we subsequently wished to evaporate gold, the Si/SiO_2 surface was modified with an adhesion-layer self-assembled monolayer (SAM) of mercaptopropyl trimethoxylsilane (MPTMS) via vapor deposition prior to TP. We found that amino- or carboxylic-group-terminated SAMs could also result in good TP of the inorganic salts and the printing results on these surfaces are indistinguishable from those on thiol-modified substrates. After lifting the stamps, a thin film of salt was transferred to the Si/SiO_2 surface. In all cases, the PDMS stamps were clean after printing, as far as could be determined optically. We reused the same stamps for printing several times and did not find deterioration of the printed features.

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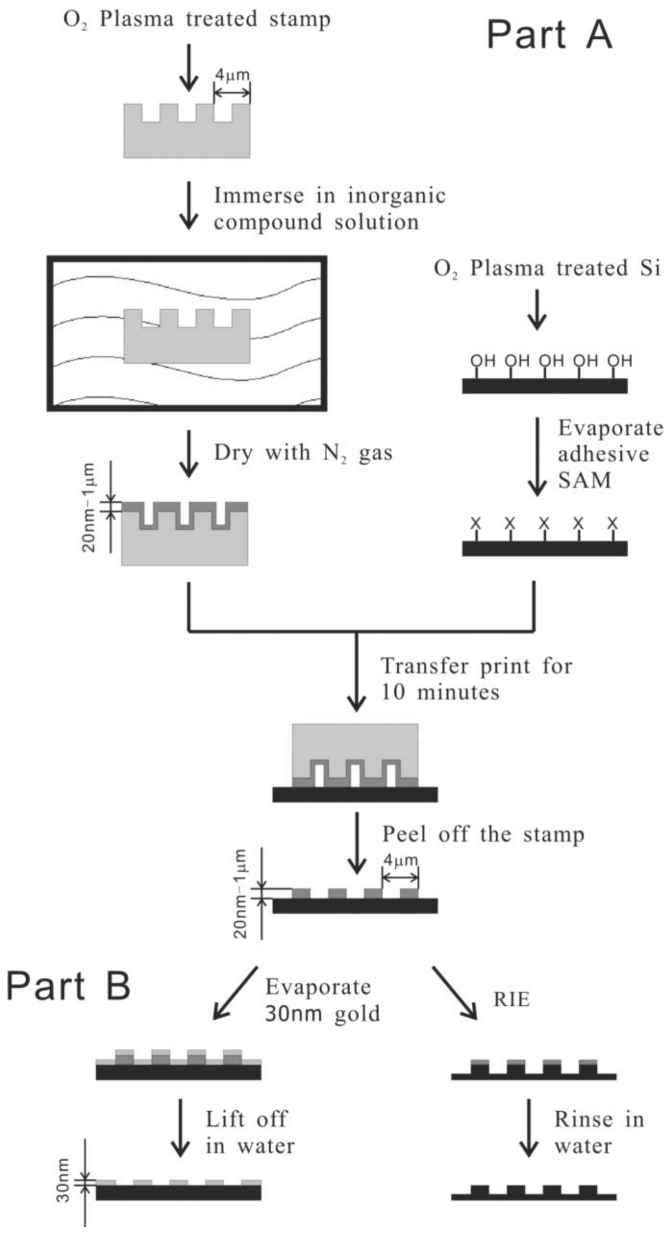

Figure 1. Schemes of the TP process (Part A) and using the patterned salt as a water-soluble template for lift-off process or reactive-ion etching (RIE; Part B). SAM: self-assembled monolayer.

Figures 2a–c show the atomic force microscopy (AFM) images and their cross-section analyses of transfer-printed $CuSO_4$. We found that the concentration of the $CuSO_4$ solution affected the TP result: Using the same stamp with a line pattern and following the same patterning procedure (2 h immersion and 10 min TP), $CuSO_4$ beads (Fig. 2a) were left on the Si/SiO_2 surface at low concentration (30 mM), while $CuSO_4$ lines (Fig. 2b) were transferred with high fidelity at high concentration (0.2 M). When the $CuSO_4$ concentration was further increased to 0.4 M (Fig. 2c), the patterns broadened due to "overinking". When we used a NaOH solution (375 mM) or NaOH solution with sodium dodecyl sulfate (SDS) (0.17 mM), no uniform line pattern was transferred (Figs. 2d,e). We then investigated TP of a mixed aqueous solution containing 30 mM $CuSO_4$, 375 mM NaOH, and 0.17 mM SDS (this solution would be part of a copper electroless plating bath had formaldehyde been added). SDS was needed in order to prevent precipitation of salts. Following the same TP process above, uniform lines of ~300 nm in height were transferred (Fig. 2f). The salt patterns adhered very strongly to the MPTMS monolayer and easily passed a so-called "Scotch tape" adhesion test. Similarly, KNO_3 (Figs. 2g,h) and a mixture of KNO_3 and KOH (Fig. 2i) were transfer-printed on an MPTMS Si/SiO_2 surface. Scanning electron microscopy (SEM) images (Fig. 3) show the high quality of the printed salt patterns. It is possible to control the thickness of the salt pattern by varying the immersion time of the stamp in the salt solution. We were able to deposit salt films with thicknesses ranging from the submicrometer scale (~800 nm) (Figs. 3a,b) to the nanoscale (~20 nm) (Figs. 3c,d) by simply changing the immersion time from 4 to 1 h.

Apart from the salts above, K_2CO_3 (Fig. 4) has also been patterned using TP. The stamp-inking procedure in this experiment was slightly different: one drop of a saturated K_2CO_3 solution in methanol was placed on top of an O_2-plasma-oxidized PDMS stamp and dried by slow evaporation (~1 h). Subsequently, the K_2CO_3 film was transfer printed in the same way as the transfer-printed KNO_3. Figures 4a–c show very well-aligned K_2CO_3 islands, which have a period of 4 μm, diameter of 0.8 μm, and height of 280 nm. The energy dispersive X-ray (EDX) spectra in Figures 4d,e confirm the transfer of K_2CO_3 only to those areas that were in contact with the stamp.

To further characterize the composition and morphology of some of the printed layers, we used X-ray diffraction (XRD) and Auger electron spectroscopy (AES). The XRD spectrum (Fig. 5a) shows that the $CuSO_4$ formed a highly crystalline layer, which corresponds to the XRD database spectrum of $CuSO_4{\cdot}5H_2O$. Since no obvious crystal structure was observed under an optical microscope or a scanning electronic microscope, we believe that the $CuSO_4{\cdot}5H_2O$ crystals are very small and that they can pack tightly together to follow the stamp topography.[32]

The $CuSO_4$/NaOH mixture resulted in nice patterns, but elemental surface analysis with AES showed only the presence of Na and O and not Cu on the sample. Furthermore, the XRD spectrum (Fig. 5g) shows the presence of neither a crystalline pattern nor an amorphous ridge in this sample (even after long scanning times of 20 s per step). We believe that, in this case, an amorphous NaOH film transferred, with the amorphous ridge so weak that it overlapped with the baseline. Considering that there was a 12-fold excess of NaOH over $CuSO_4$, we speculate that only the NaOH nucleated on the PDMS stamp and that the amount of $CuSO_4$ in the transferred salt layer was below the detection limit of AES. The XRD spectra in Figures 5b–d show the (micro)crystalline nature of the printed potassium salts.

The inorganic salts were then used as water-soluble masks for microfabrication. Currently, commercially available resists

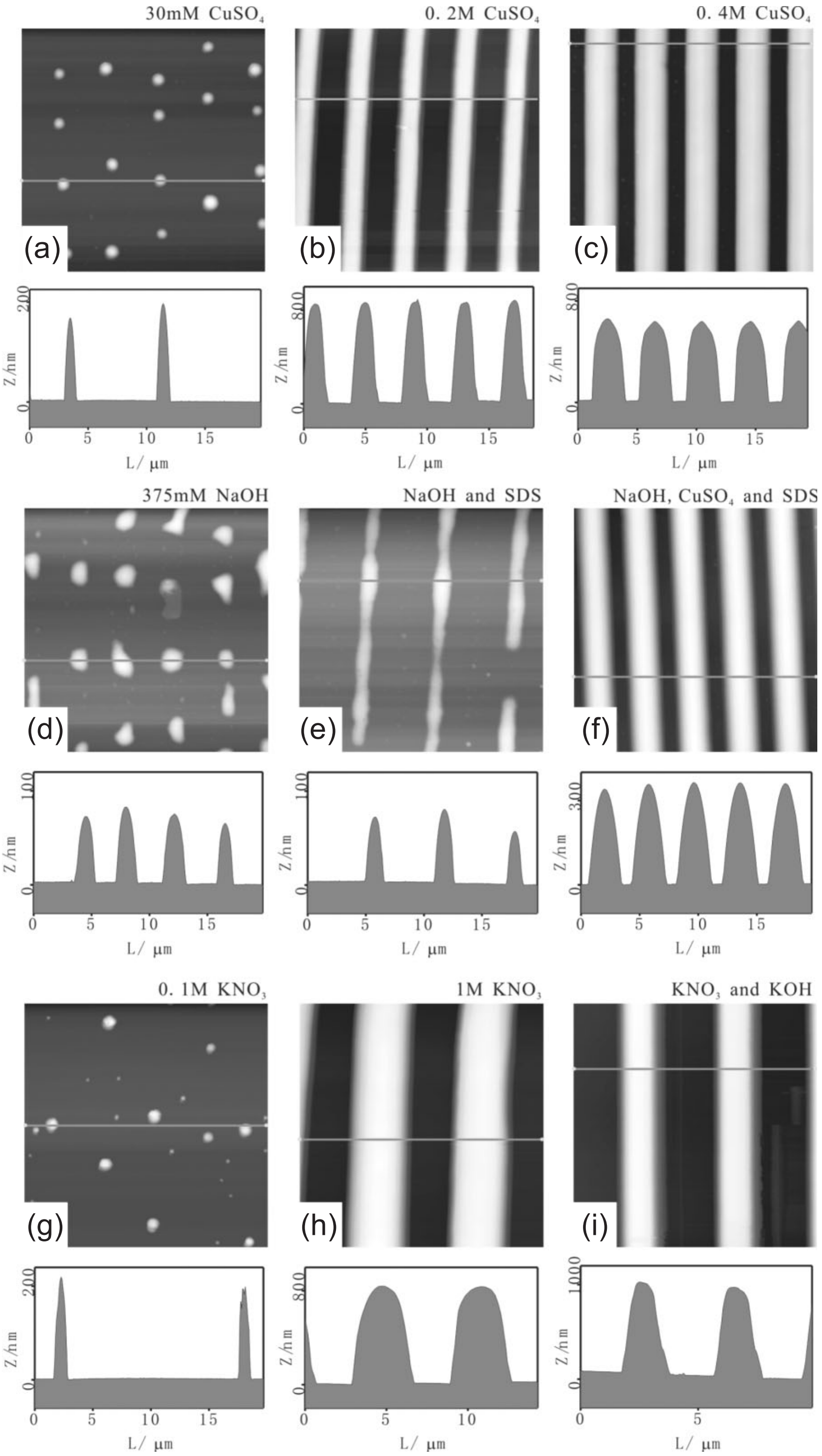

Figure 2. AFM topographic images and cross-section analyses of transfer-printed inorganic salt patterns. An oxidized PDMS stamp with a line-shape pattern was immersed in a a) 30 mM $CuSO_4$ aqueous solution, b) 0.2 M $CuSO_4$ aqueous solution, c) 0.4 M $CuSO_4$ aqueous solution, d) 375 mM NaOH aqueous solution, e) 375 mM NaOH/0.17 mM SDS aqueous solution, f) 375 mM NaOH/30 mM $CuSO_4$/0.17 mM SDS aqueous solution, g) 0.1 M KNO_3 aqueous solution, h) 1 M KNO_3 aqueous solution, and i) 110 mM KNO_3/375 mM KOH aqueous solution at 55 °C for 2 h (4 h for (i)). The stamp was then dried using a N_2 gun and printed on a piece of MPTMS-coated Si wafer for 10 min. After removing the stamp, salt patterns were left on the Si wafer. The corresponding height profile beneath each image was measured along the line shown in the image (*L*: distance; *Z*: height).

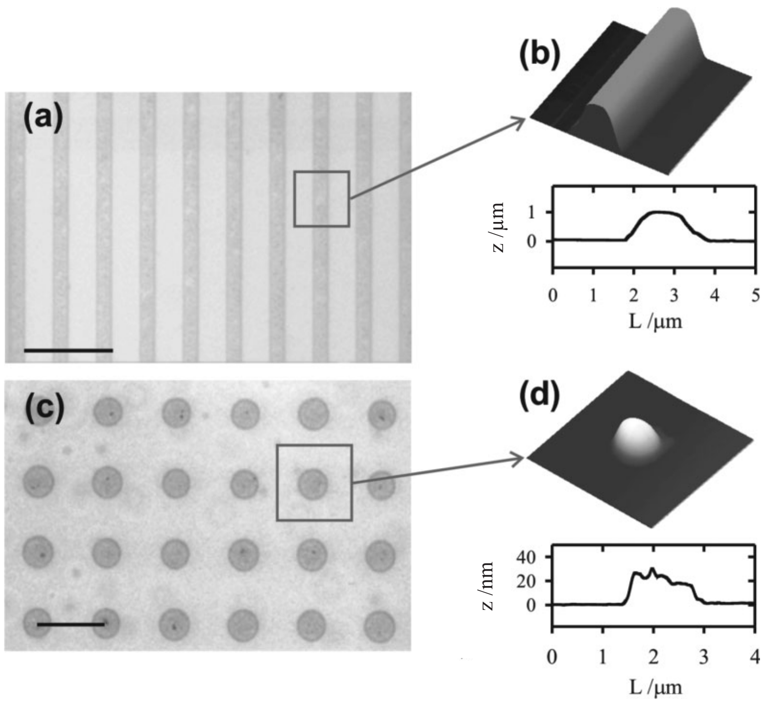

Figure 3. a) SEM image of patterned KNO_3 lines (scale bar: 8 µm); b) Three-dimensional (3D) AFM image of the pattern shown in (a) and its corresponding cross-sectional analysis; c) SEM image of patterned KNO_3 dots (scale bar: 4 µm); d) 3D AFM image of the pattern shown in (c) and its corresponding cross-sectional analysis.

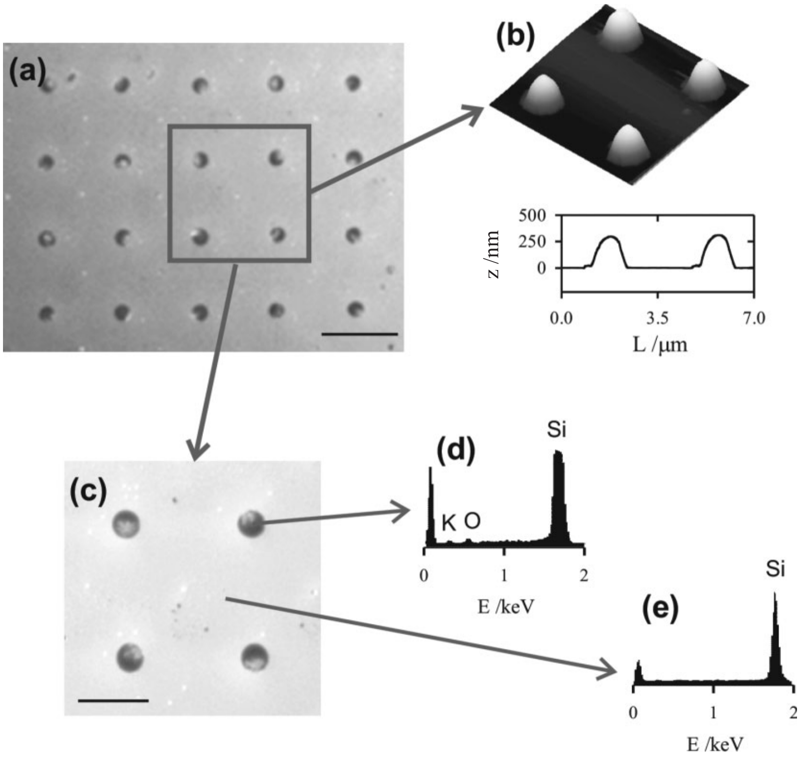

Figure 4. a) SEM image of patterned K_2CO_3 dots (scale bar: 4 µm). b) 3D AFM image of (a) and its corresponding cross-sectional analysis. c) Magnified SEM image of (a) (scale bar: 2 µm). d) EDX spectrum of transferred K_2CO_3. e) EDX spectrum of non-contact area while transfer printing.

generally involve the use of hazardous solvents such as ethylene glycol and cyclohexanone in addition to the use of corrosive aqueous solutions like tetramethyl ammonium hydroxide. In clear contrast, using water as a "developer" involves the use of not only an environmentally friendly, but also a low-cost solvent. The application of inorganic salts as water-soluble masks is demonstrated below. Figure 6a shows a 250 nm thick transfer-printed NaOH film with 4 µm period holes, which are 8 µm in diameter. This patterned surface was used as a water-soluble template for gold evaporation. A thin film of gold (30 nm) was thermally evaporated at 0.1 nm s^{-1} onto the as-made NaOH patterned Si wafer (previously coated with MPTMS). The sample was then ultrasonicated in MilliQ water for 20 min to remove the salt layer and lift off the gold on top. Figure 6b shows an SEM image of incomplete lift-off of the gold film; Figures 6c,d show SEM and AFM images, respectively, of the final remaining gold islands. The smooth top surfaces and the sharp sidewalls of the gold islands (Fig. 6d) and the accurate reproduction of the NaOH holes and gold islands indicate that the water-soluble template can be used as a mask/resist for precise patterning. Gold lines on Si (Fig. 6e) were also fabricated by the same procedure.

The NaOH pattern was also used as a water-soluble mask for reactive-ion etching (RIE). A Si wafer with a NaOH pattern was place in the RIE chamber. The chamber was sealed, brought under vacuum, and filled with CF_4 gas, after which a plasma was formed. The etching process was carried out under different plasma powers and CF_4 pressures. Finally, the etched sample was fully rinsed with MilliQ water. Figures 7a–c show an etched Si surface (40 W and 0.4 mbar; 1 mbar = 100 Pa) that had been protected by a 200 nm thick NaOH mask. The Si with NaOH on top was well protected from etching, giving a roughness of 1 nm, as determined by AFM analysis. In contrast, the unprotected Si area was attacked by the CF_4 plasma and formed 150 nm deep trenches after 5 min etching, giving a roughness of 4 nm. The smooth and vertical sidewalls indicate not only anisotropic etching during the RIE process, but also that NaOH is a very good resist as no CF_4 plasma penetration occurred. Only at very long etching times (> 10 min) did we find degradation of the NaOH salt layer. This result shows that NaOH is a superior resist material compared with the normally used AZ photoresists which have about 0.3–0.7 times faster etching speeds (under CF_4 plasma) than Si.[33]

The etching property of NaOH was further utilized for fabricating micropatterned Si with nano-

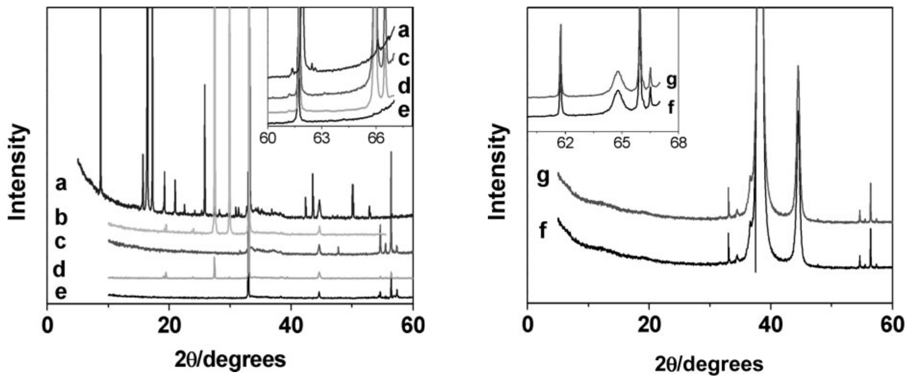

Figure 5. XRD spectra of patterned surfaces from printing with a) $CuSO_4$ on Si, b) KNO_3 on Si, c) K_2CO_3 on Si, d) a KNO_3/KOH mixture on Si, and g) a $CuSO_4$/NaOH/SDS mixture on gold, e) a Si <100> wafer, and f) 200 nm Au (plus 15 nm Cr) evaporated on Si <100>.

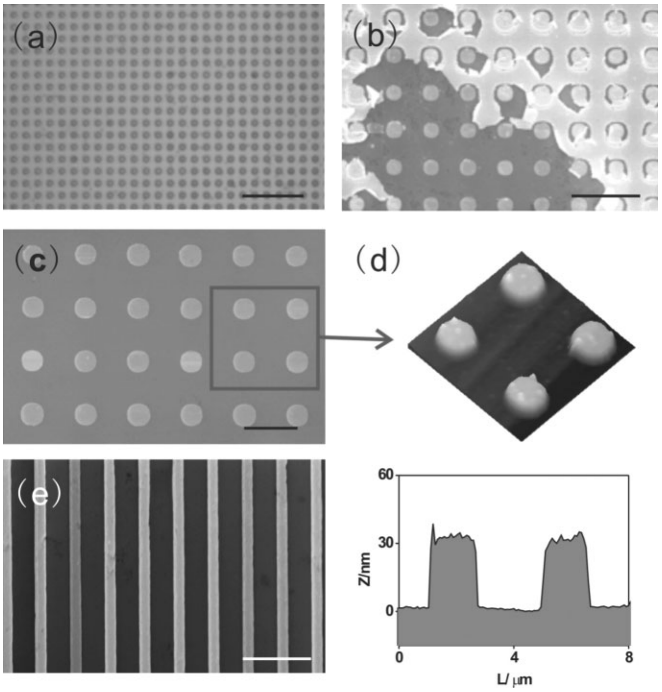

Figure 6. a) Optical microscopy image of patterned NaOH holes (scale bar: 20 μm). b) SEM image of gold pattern in the process of lift off (scale bar: 8 μm) using (a) as the water-soluble template. c) SEM image of gold pattern after being lifted off (scale bar: 4 μm). d) 3D AFM image of (c) and its corresponding cross-sectional analysis (below). e) SEM image of gold lines fabricated using the same procedure as (c) (scale bar: 8 μm).

scale surface roughness. A 5 nm thick NaOH feature was transfer printed on a Si wafer, following by RIE in CF_4 plasma (60 W, 0.2 mbar) for 3 min and rinsing with MilliQ water. The result is shown in Figures 7d–f. In this experiment, the NaOH layer was very thin and did not act as a good resist, which resulted in breakthrough in the protected areas, leading to a micropatterned Si (Fig. 7d) with nanoscale (20 nm) surface roughness (Fig. 7e). The edge resolution is also very high, as shown in Figure 7f. The edge roughness should be caused by the stamps from which the molds were fabricated by photolithography. This etched Si may be potentially used as substrate of (responsive) superhydrophobic surface, in which a rough substrate with microscale pattern is the precondition.

3. Conclusion

In conclusion, we report the first example of the fabrication of KNO_3, K_2CO_3, $CuSO_4$, NaOH, and salt-mixture (KNO_3 and KOH) patterns using the TP technique. The concentrations of salt solutions were found to be a key issue for good pattern transfer. By varying the immersion time, it is possible control the height of the raised features of the TP salts from the nanoscale to the submicrometer scale. Utilizing these inorganic salts as water-soluble masks for micromachining was demonstrated. A TP patterned NaOH film was used as a water-soluble template for the preparation of patterned gold films via evaporation of a thin layer of gold on top of a patterned salt resist and subsequent development via ultrasonication in water. The results show precise matching of the sizes between the NaOH holes and gold islands and very sharp sidewalls on the gold islands, which indicate that this indirect lithographic method has large potential for use in micro- (and nano-) lithography. Furthermore, NaOH was used as a water-soluble mask for reactive-ion etching. By controlling the thickness of NaOH and the etching conditions, we fabricated either Si structures with very low surface roughness or Si micropatterns with nanoscale roughness; the latter may be suitable for the fabrication of superhydrophobic surfaces or for cell-adhesion studies. The use of water as a developer solvent indicates the potential utility of the patterning of inorganic salts as a low-cost, simple, and, more importantly, environmentally friendly route towards accurate patterning of different materials. Finally, our method presents a potential route to patterning polymeric substrates that could otherwise be damaged using organic solvents to develop or rinse off photoresist.

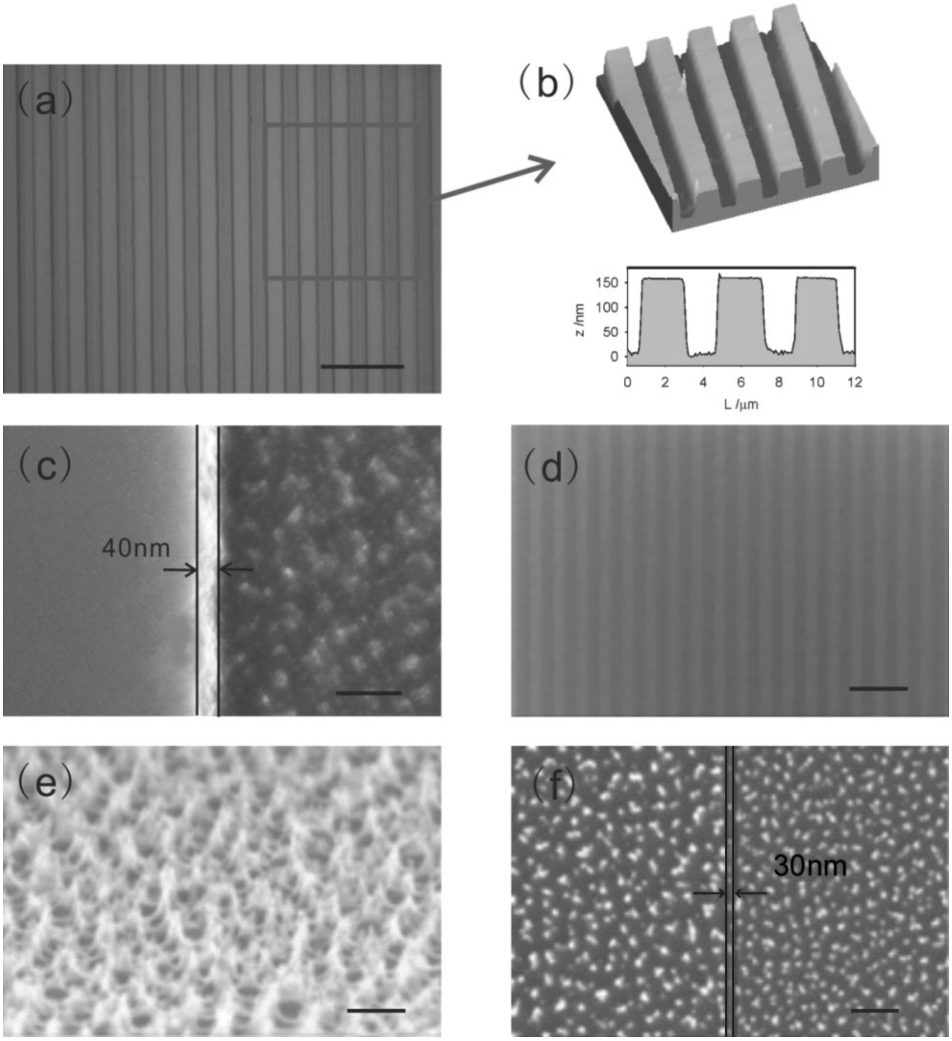

Figure 7. a) Optical microscopy image of Si patterned by RIE (scale bar: 10 μm). The Si was covered with a 200 nm thick NaOH layer feature before being etched. b) 3D AFM image of (a) and its corresponding cross-sectional analysis. c) A magnified SEM image of (a), showing its edge resolution (scale bar: 200 nm). d) SEM image of Si patterned by RIE (scale bar: 10 μm). The Si was covered with a 5 nm thick NaOH feature before being etched. e) A magnified tilted SEM image of (d) showing the nanoscale-rough surface (scale bar: 400 nm). f) A magnified SEM image of (d), showing its edge resolution (scale bar: 200 nm).

4. Experimental

PDMS-Stamp Fabrication: Prepolymer Sylgard 184 and its curing agent were mixed in a ratio of 10:1 and then cast on a photoresist master patterned by photolithography. After cured at 65 °C for 24 h, the PDMS stamp was peeled off from the master.

Modification of Substrate: Shown in Figure 1 (Part A right), a clean silicon wafer was ultrasonicated in acetone, isopropanol, and MilliQ water for 5 min, respectively. It was then dried with N_2 gas and O_2-plasma oxidized for 10 min to render the –OH groups on the surface. In the case of making MPTMS-coated Si, the oxidized Si wafer was placed in a vacuum chamber with 3-mercaptopropyl trimethoxylsilane hexane solution (one drop of 3-mercaptopropyl trimethoxylsilane in 2 mL of hexane) for 3 h, followed by baking at 80 °C for 1 h. In the case of amino-terminated SAMs, aminol propyl trimethoxysilane (APTS) was used. For preparation of the carboxylic groups, a piece of clean gold (200 nm of gold evaporated on Si with 15 nm of Cr in between) was immersed in a 5 mM 16-mercaptohexedacanoic acid solution in ethanol for 24 h, followed by rinsing in fresh ethanol and drying under N_2.

Gold Evaporation: The gold evaporation was done using an EDWARDS AUTO500 thermal evaporator. The salt-patterned sample was placed upside down in the vacuum chamber overnight before evaporation. The evaporating speed was 0.1 $\text{nm}\,\text{s}^{-1}$ and the chamber vacuum was kept at 10^{-7} Pa during the evaporation.

XRD Measurements: XRD measurements were carried out on a Philips vertical diffractometer, with a Cu Kα X-ray source and a second graphite monochromator. The inorganic salts were patterned on either gold or Si substrates and molded on the XRD sample holder for measurement. For KNO_3 sample, the step size was 0.05° with 5 s scanning per step. For the other samples, the step size was 0.03° with 20 s scanning per step.

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