

Patterning colloidal suspensions by selective wetting of microcontact-printed surfaces

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Abstract

Micropatterns made of ceramic powders can be obtained by selective wetting of microcontact-printed surfaces. A large wetting contrast between hydrophilic micropatterns and hydrophobic areas was created. Aqueous colloidal dispersions of aluminum oxide and tin oxide adhered only to the hydrophilic micropatterns whereas they were repelled from the hydrophobic areas in a simple dip coating process. We examined two molecular ink/substrate systems: thiol self-assembled monolayers (SAM) on gold and octadecyl-trichlorosilane (OTS) SAM on silicon wafer substrates. Corresponding contact angles obtained under varying printing conditions are presented. The chemical compositions of the printed layers were characterized by ToF-SIMS mass spectrometry. The thiol-gold SAM readily forms in microcontact printing whereas the OTS layer contains a significant amount of PDMS residues. However, printing and selective wetting could be carried out successfully on both ink/substrate systems. The ceramic micropatterns obtained indicate a maximum resolution in the order of 5 μm .

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1. Introduction

Microcontact Printing (μCP) is an extremely versatile alternative to standard photolithography for direct micropatterning of a variety of substrates. It was introduced as one of a whole set of techniques for alternate microfabrication (Soft Lithography) using elastomeric molds for pattern transfer.¹ Elastomeric stamps are easily prepared by casting a prepolymer of polydimethylsiloxane (PDMS) against the topography of a master structure which themselves may be prepared by photolithography or other microfabrication methods. The stamps containing recessed microstructures are inked and subsequently brought into contact with substrates to transfer molecules in micropatterns by a simple printing process (Fig. 1a). The best characterized ink system is the printing of alkylthioles that form self-assembled monolayers (SAM) on gold surfaces.^{2,3} The SAM may be used as an ultimately thin mask for etching the gold layer selectively.^{4,5} This has been demonstrated by using μCP for creating microelectrodes

for cyclic voltammetry.⁶ The achievable resolution may be in the submicron range, even on large areas.⁷ Substrates do not necessarily need to be flat, as the work of Jackman et al. demonstrates.⁸ Other printable substances include an enormous range of both ink and different substrates, for instance the printing of Pd catalysts for electroless deposition of patterned metal films,⁷ zeolite layers⁹ or biofunctional layers like patterned protein repellent polylysine-polyethyleneglycol co-polymers for cell adhesion studies.^{10,11} Protein microarrays have also been presented.¹² Since μCP can be carried out without clean room equipment, the method is spreading quickly among various disciplines. One of the most striking features of μCP is the possibility to scale up the process for continuous mass fabrication since the process is the microfabrication equivalent of printing on paper. The group of Michel at IBM Corporate Research has undertaken first steps in that direction,^{13,14} thereby synthesizing more rigid PDMS-analog elastomers than the commercially available standard blend.¹⁵

In this article, we propose to supplement μCP with a scheme for the microfabrication of ceramic thick films. We use μCP for generating contrasting hydrophilic and hydrophobic areas which are then selectively wetted by

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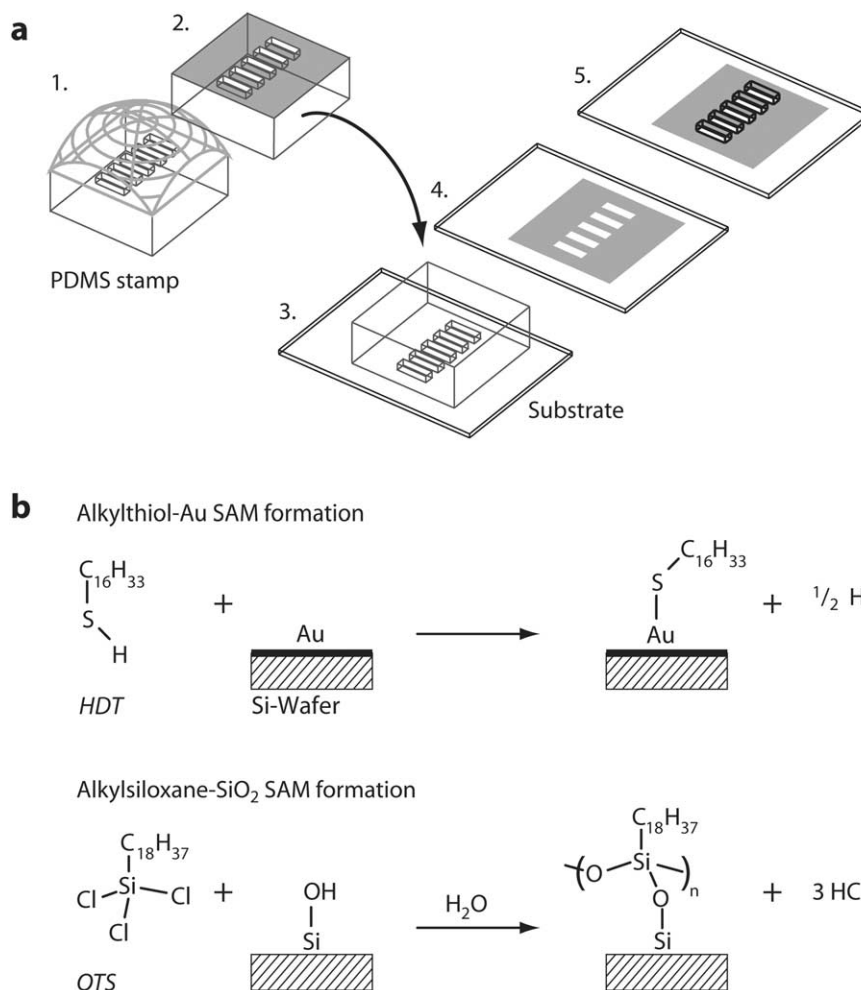


Fig. 1. (a) Principle of microcontact printing: (1) PDMS stamp is inked with a SAM-forming molecule in solution and (2) dried; (3) the stamp is brought into contact with a substrate; (4) transferring its pattern by forming the SAM; (5) substrates are then coated with colloidal suspensions by dip coating, yielding a surface with micropatterned thick film coatings. (b) Reactions of SAM formation with hexadecanethiol (HDT) on gold and octadecyltrichlorosilane (OTS) on SiO₂ surfaces.

a colloidal suspension to form micropatterns of ceramics. The article is part of a series in which other Soft Lithography techniques have been used to fabricate small elements of ceramic powders.^{16–20} Powders may offer several advantages over standard thin film ceramics, e.g. higher sensitivity and controlled porosity for gas sensing applications.^{21,22} We examine two ink/substrate systems, the thiol–gold and the metal-less alkanetrichlorosilane chemistry which allows to print directly onto bare silicon wafer substrates, see Fig. 1b. The layers obtained by μCP have been characterized by water contact angle measurements and more sensitively by ToF-SIMS (time-of-flight secondary ion mass spectrometry).

2. Experimental

The masters containing a positive relief of the mold structures were prepared by standard photolithography

using AZ4562 positive resist (Clariant GmbH, Wiesbaden, Germany). Nine grams of Sylgard 184 PDMS prepolymer/catalyst mixture (Dow Corning Inc., Midland, MI, USA) were poured over a master structure and cured for 26 h.

The substrates were silicon wafer pieces with a freshly evaporated layer of gold prepared by thermal evaporation in a Balzers MED 020 system at 1.7×10^{-5} mbar, thickness ranging from 10.3 to 33.7 nm, including a layer of Cr (thickness 6.7 nm) in between to promote adhesion. For direct printing of octadecyltrichlorosilanes, bare Si wafer pieces were cut, rinsed with water (18 M Ω cm, Millipore), cleaned in an ultrasonic bath and subsequently treated in an oxygen plasma sterilizer for 2 min (Harrick PDC-32G).

2.1. μCP on Au layers

The PDMS stamp was inked for 30 min in 25 ml of 1-hexadecanethiol HDT solution (Fluka AG, Buchs,

Switzerland, used as received) in ethanol (38 μl HDT in 25 ml EtOH, 5 mM). After this time the stamp was taken out of the solution and dried with a stream of nitrogen. Then it was placed on the substrate for 20 s before being removed. The printed substrate was immersed in a 25 ml solution of cysteamine hydrochloride $\text{HS}(\text{CH}_2)_2\text{NH}_2\text{HCl}$ (Fluka) in ethanol (0.014 g cysteamine hydrochloride salt in 25 ml EtOH, 5 mM) for 30 min, after which it was removed, washed in ethanol and dried with a stream of nitrogen.

2.2. μCP on Si

A 5 mM solution of octadecyltrichlorosilane (OTS) (Fluka) in either hexane or ethanol was prepared just minutes before printing. Microcontact printing was carried out the same way as detailed above, with a contact time of 60 s. The substrates were heated to 60 °C for 15 min and then rinsed thoroughly with the solvent in use.

2.3. Al_2O_3 suspensions

The suspensions of powders with Al_2O_3 of 190 nm median particle size, 45 vol.%; Taimai Industries, Tokyo, Japan, TM-DAR 2831, (27.87 ml) were prepared by adding the powder to an aqueous solution of NH_4Cl (0.0745 g, 1.39 mmol, 0.05 M) and HCl (2 M, Titrisol, Fluka). An arbitrary amount of HCl was used here to reduce the pH of the suspension into the region 4–5. This suspension was ball milled overnight before use.

2.4. SnO_2 suspensions

A quantity of 21.1 g Tin oxide powders (220 nm median particle size, 33 vol.%; Cerac Inc., Milwaukee, WI, USA) was added to 6.01 g of water containing 150 μl of dispersing agent which was prepared by mixing 6.65 g water, 1.84 g polyacrylic acid sodium salt 2100 (Fluka) and 0.06 g NH_3 , 25% in H_2O . Again, the suspensions were homogenized by ball milling sequences throughout the powder adding procedure.

2.5. Coating the printed substrates

The substrates were coated with suspension either by dip-coating or by dropping the suspension onto a tilted substrate (tilt angle approx. 70°). Sintering was done by heating the samples in air to 800 °C for 5 h in the case of SnO_2 microcoatings, resp. 1100 °C for 2 h for Al_2O_3 coatings.

2.6. Surface characterization

The static contact angle of water was determined on all samples. ToF-SIMS mass spectrometry was carried out in a PHI 7200 analyzer using a Cs^+ primary ion

beam with an incident energy of 8 keV. Samples were microcontact-printed not more than 3 h before measurement using blank PDMS stamps without microstructures. Reference samples were prepared by immersion in the ink solutions over night for the full SAM coverage references, and treating bare Si, resp. Au-coated pieces only with oxygen plasma for the blank reference samples. The ion dose was below the static limit ($< 1.0 \times 10^{12}$ ions/ cm^2). The primary ion beam was scanned over an area of $200 \times 200 \mu\text{m}^2$. Acquisition pulses were of 1.25 ns duration with an acquisition time of 1.7 min/spectrum. Typical $m/\Delta m$ resolutions obtained ranged from 3000 to 5000. The spectra were fine-calibrated with the PHI Tofpak software using the exact masses of a standard set of small ions.

3. Results and discussion

The alkanethiol and alkanetrichlorosilane molecules shown in Fig. 1b are used to create the hydrophobic surfaces. In the case of gold–thiols, the unprinted regions had to be backfilled with another thiol, cysteamine hydrochloride $\text{HS}(\text{CH}_2)_2\text{NH}_2\text{HCl}$, forming the hydrophilic layer with its ammonia head groups. The substrates were then dip-coated in 45 vol.% alumina suspensions, resulting in the coating of the line pattern after drying as shown in Fig. 2a (dark lines are ceramic, gold is bright). Atomic force microscopy (AFM) cross-sections of the resulting ceramic coatings are displayed in the insets. The rounded shapes are a combined result of the contact angle of wetting, the surface tension of the suspension, the drying shrinkage and minor AFM tip shape influence (sidewalls of a single pit on a compact disc could be well resolved with the same type of tip). For a given micropattern geometry, the height of the coating can be influenced by the suspension properties. The addition of NH_4Cl to the suspension was crucial. Without salt, the suspension did not selectively wet the patterned substrate, only a dense, continuous layer was formed. When added to pure water, salt increases the surface tension of the solution slightly. In order to get a rough estimate of the change of the surface tension of alumina suspensions by the NH_4Cl addition, the weight of suspension droplets generated with a pipette was measured. The surface tension σ of a liquid is related to the weight of a droplet $V\rho g$ and the radius of the pipette tip r_c .²³

$$V\rho g = 2\pi r_c \sigma \quad (1)$$

The surface tension of an alumina suspension is significantly lowered by the salt addition from 8.8×10^{-2} N/m to 3.9×10^{-2} N/m. A lower surface tension is favorable for the wetting process. The contact angles of water on the surfaces prepared in this work are summarized in Table 1. In the thiol–gold system, a contact angle difference of alkanethiol/cysteamine SAM layers

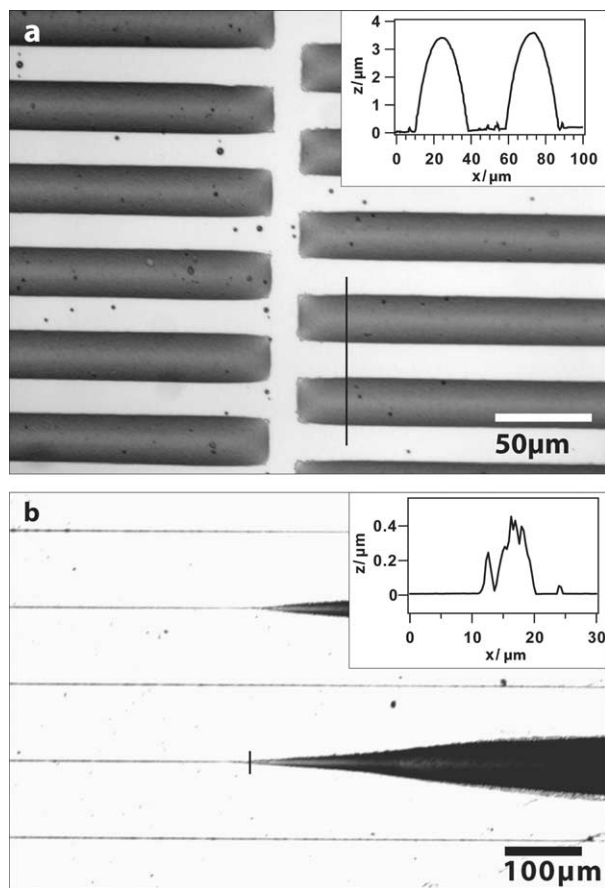


Fig. 2. (a) Micropatterned ceramic lines of 20 μm width on gold substrates; (b) resolution test structure of triangles that narrow down to form 5 μm wide lines. These thin lines are reproduced with estimated deviations of approximately 1–2 μm .

Table 1

Summary of measured water contact angles θ , which were measured in static mode; where available, values ($^\circ$) are presented as range over several samples

Surface treatment, θ_{water}	PDMS	Au substrate	Si substrate
PDMS, plain	110		
PDMS, O ₂ plasma-treated	<2		
Au, plain		76	
μCP , Au–HDT SAM ^a		108	
Au–HDT from EtOH solution		105	
μCP , Au–cysteamine HCl		43–46	
Si as received			33–36
Si O ₂ plasma-treated			<2
μCP , OTS/hexane ink			95–110
μCP , OTS/EtOH ink			99–104
OTS from hexane solution			99
μCP , PDMS dry			60–67

^a μCP ,... = surface prepared by microcontact printing using PDMS stamps and the ink/substrate combination as indicated.

of approx. 65° is reached. This contrast is sufficient for selective wetting of colloidal suspensions.

In Fig. 2b, another ceramic coating of a triangular test pattern demonstrating the resolution capabilities of

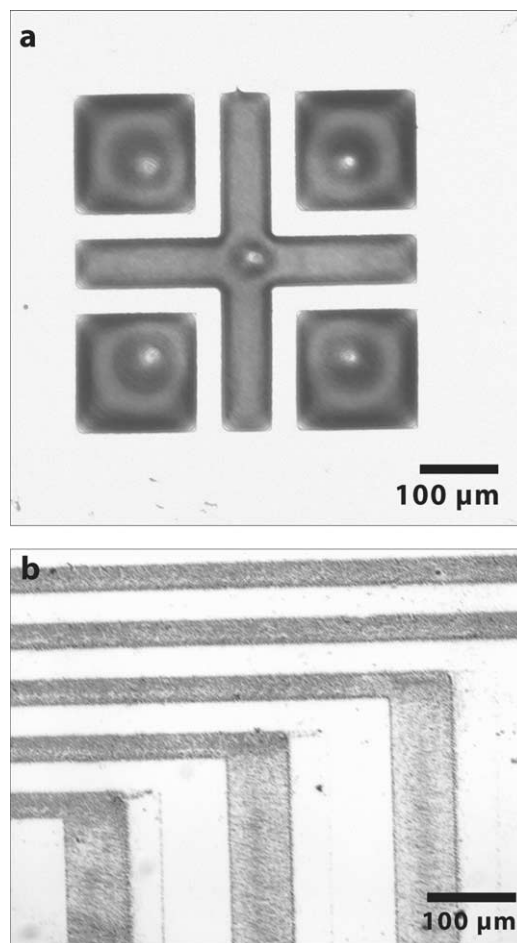


Fig. 3. (a) Cross structure of tin oxide formed by the OTS/Si μCP approach; (b) 20 μm tin oxide line pattern coated on Si wafers.

the process is shown. This sample was prepared by droplet deposition. The triangles narrow down to lines of 5 μm width which are clearly resolved with a contiguous layer of a few particles. However, the edges of the triangles are not always resolved sharply. When looking closely at the hydrophobic/hydrophilic boundary, fractal-like or dendritic structures are observed. This is probably due to the backfilling process during which cysteamines may have partially substituted alkanethiols.

In the case of the alkanetrichlorosilane approach, a backfilling is not needed since the silicon surface is very hydrophilic after the oxygen plasma treatment. However, the surface chemistry is more complicated. The SiCl_3 functional group is much more reactive than SH and can readily polymerize in presence of small amounts of water like air humidity. And, as indicated in Fig. 1b, water is necessary for covalently linking the trichlorosilane head group to silicon oxide. Usually, such OTS layers are used for friction reduction in silicon-based MEMS devices. They are coated with OTS from solution in a dry solvent such as hexane.^{24,25} The heating step to 60 °C was suggested for completing the

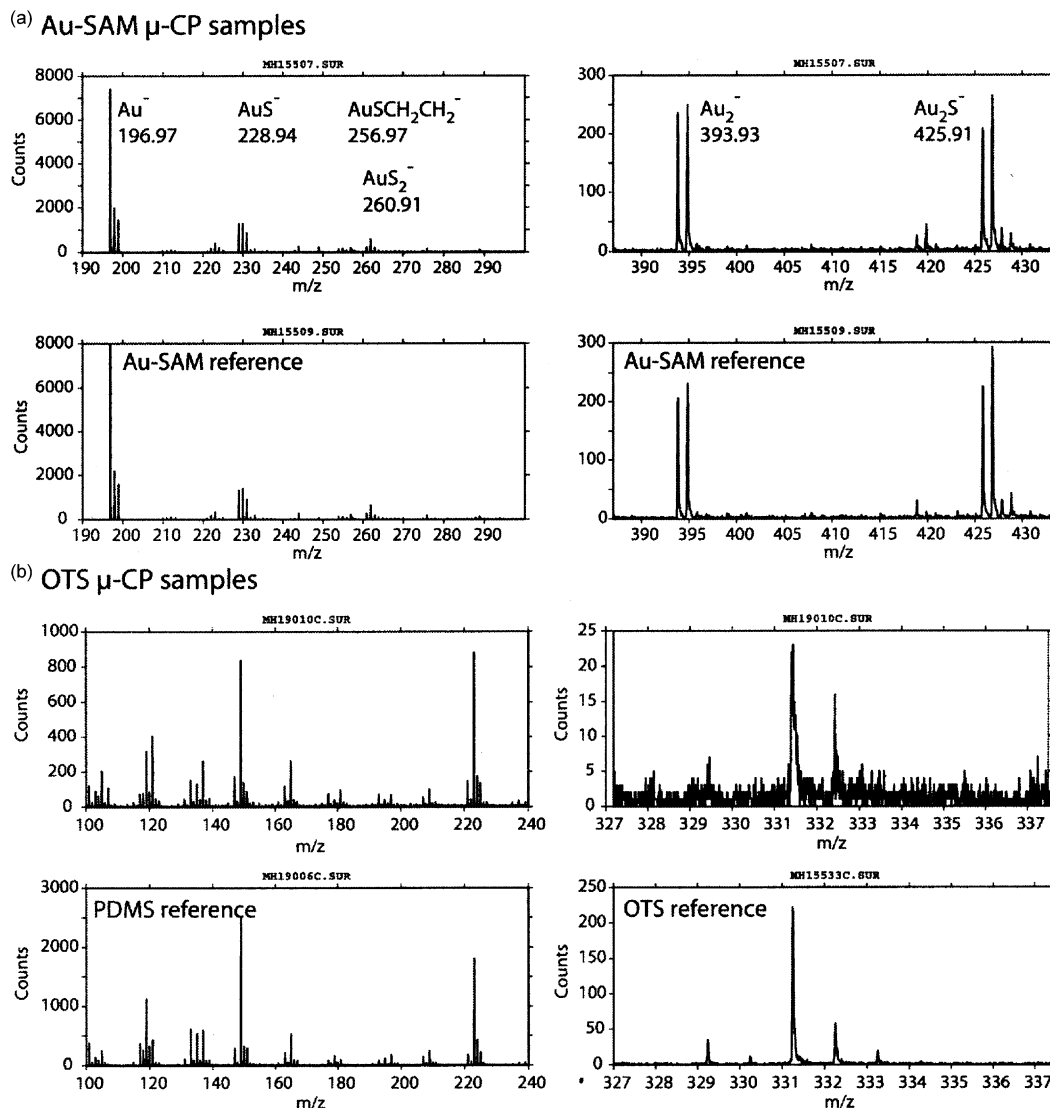


Fig. 4. (a) Negative mode ToF-SIMS mass spectra of microcontact-printed HDT on Au at various scales compared to their respective reference samples (below); (b) ToF-SIMS results from the OTS-SiO₂ system.

cross-linking reaction. It is suggested that the surfaces under ambient conditions contain enough adsorbed water for cross-linking OTS to a SAM. Jun et al. circumvent this problem by treating the silicon surface with chlorine, then printing octadecanol.²⁶ The main drawback of this approach is the need for an inert atmosphere due to the reactivity of Si-Cl species. The PDMS stamp is temporarily dried in the μ CP process. Interfering reactions of water from PDMS surfaces or air with OTS may occur before SAM formation on the surface. Therefore, it is not clear whether a well ordered SAM is formed under typical microcontact printing conditions. Experiments in which PDMS was immersed for a few minutes in hexane showed that PDMS is damaged by swelling and extraction of components by the solvent. PDMS loses its ability to spontaneously seal smooth surfaces and becomes white-opaque and

brittle. Therefore, it was decided to use ethanol as solvent for OTS. A contrast in water contact angle of up to 71° could be created in spite of these suspected side reactions (Table 1). Ceramic microcoatings of 33% tin oxide suspensions could be formed successfully by dip-coating (Fig. 3a), respectively droplet coating (Fig. 3b). When printing structures in the 100 μ m range, the suspensions dry unevenly and form shallow holes in the center of the coated surfaces.

Sintering of the microcoatings was performed up to 1100 °C without cracking the layers. However, the oxidation of silicon has to be taken into account. Under wet oxidation conditions, the ceramic layer can partially be embedded in a SiO₂ layer. If the Au layer is thicker than 100 nm, delamination of the ceramic microlines may occur due to the gold coalescing into droplets. This delamination can be avoided using thinner gold films

around 30 nm. This effect could also be used deliberately for separating ceramic parts from its substrate support.

In order to learn more about the composition of these hydrophobic layers, ToF-SIMS measurements were performed on microcontact-printed silicon and gold surfaces. Since alkanes do not form many stable anions whereas Au and Sulfur-containing species do, the negative mode mass spectra yielded more information. ToF-SIMS measurement data of alkanethiol SAMs on Au have been published before.²⁷ Mass spectra of μ CP HDT–Au samples are compared to a reference SAM in Fig. 4a. A good match was obtained, there are no obvious differences. The formation of various AuS-fragments proved very useful for direct confirmation of a sulfur–gold chemical bond. Minor amounts of PDMS were also detected.

Microcontact-printed OTS layers on Si are not as easily identified as in the case of gold–thiol SAMs. The layer is of similar composition as the substrate. Si possibly originates from the wafer, its native SiO₂ layer, from PDMS and from OTS. Cl is expected to evaporate as HCl during the coating process and general alkane signals are too unspecific for identification of OTS. Therefore, the only mean to establish the presence of an OTS-layer unambiguously is the detection of intact octadecyltrioxysilane species, e.g. $m/z = 329$ (SiO₃(CH₂)₁₇CH₃)[−] or $m/z = 331$ (H₂SiO₃(CH₂)₁₇CH₃)[−], which could be detected (see Fig. 4b). Such fragments have also been identified by Houssiau et al. who examined OTS SAM on aluminum metal surfaces.²⁸ However, the spectrum of the microcontact-printed sample strongly matches the PDMS reference spectrum. The di and trimonomeric PDMS fragment series $m/z = 119$ (CH₃Si₂O₃)[−], 133 (C₂H₅Si₂O₃)[−], 149 (C₃H₉Si₂O₃)[−], 223 (C₅H₁₅Si₃O₄)[−] are prominently present including Si isotope signals and fragments lacking H-atoms.

ToF-SIMS analysis confirmed the presence of a thiol–gold SAM with only minor amounts of PDMS contamination. In the case of transferring octadecyltrichlorosilanes by microcontact printing, there seems to be a considerable amount of PDMS residue present. The relative amount of detected OTS fragments decreased by approximately 10 times, compared with an OTS reference surface. However, these differences in chemical composition of the obtained layers do not seem to affect the macroscopic effect of selective wetting adversely. For further improvements of the method however, these findings will have to be taken into account carefully. A possible explanation for these difference to the Au–HDT system could be that OTS is able to dissolve some PDMS species which are deposited upon printing.

4. Conclusions

Microcontact printing with colloidal suspensions of ceramic powders can be successfully performed using

thiol–gold SAM and OTS–PDMS–silicon oxide chemistries. Hydrophobic/hydrophilic contrasts of up to 71° direct the wetting of the suspension, resulting in ceramic micropatterns with a maximum resolution of 5 μ m. The process is versatile for different powder dispersions, as has been shown using alumina and tin oxide colloidal suspensions. Powder-based microfabrication of ceramics has been getting increased attention recently.²⁹ This elegant and cost-effective procedure also has potential for wafer-level microfabrication.

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