Minimizing silicone transfer during micro-contact printing

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Abstract

Methods to minimize the transfer of silicone from PDMS stamps during micro-contact printing have been investigated. This study focused on amino-silanes stamped onto PTFE substrates. Analysis of the stamped surfaces was through surface sensitive techniques such as XPS and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). It was found that curing the PDMS at elevated temperatures minimized the amount of silicone transferred. The amount of silicone transferred also depended on the pretreatment of the stamp and the type of ink used.
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1. Introduction

Soft lithography techniques such as micro-contact printing have become widely used to pattern surfaces for a range of technical applications. During the micro-contact printing process, a patterned elastomeric stamp is "inked" with a solution and then brought into contact with a solid substrate. Upon removing the stamp, a pattern of "ink" remains on the surface. The choice of ink and substrate varies depending on the application, for example, alkanethiols on gold or other metals [1,2] or proteins on glass, [3,4] however, the common feature is the elastomeric stamp, usually poly(dimethylsiloxane) (PDMS).

Despite the large amount of research using PDMS stamping techniques, there is relatively little discussion about contamination issues. Graham et al., [5] studied silicone transfer using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS), two techniques particularly sensitive to surface species. The authors proposed a week long reflux and cleaning process for *each* stamp. Glasmastar et al., [6] have also investigated the problem using similar techniques for aqueous solutions on different substrates. They determined that UV/ozone treatment of the PDMS stamps

reduced the silicone transfer to a minimum and that patterned stamps transferred more silicone than flat, blank stamps. Both groups showed that silicone contamination was occurring during stamping, but few other researchers have noticed this, perhaps because surface sensitive techniques are required. Further, the patterning process is at least partially successful in the presence of silicone contamination. The amount of ink or silicones transferred depends not only on the stamping conditions (inking procedure, stamp time, stamp pressure) [5,7] but also on the condition of the PDMS stamp and the amount of volatile and non-crosslinked components [8].

A Du Pont product, Sylgard 184, is the PDMS material most commonly used in micro-contact printing. This type of PDMS is designed to cure over time and releases low molecular weight and volatile components during the process. These components can then contaminate other surfaces [8]. Plasma treating the surface of PDMS creates more silica and silicon groups and renders the surface more hydrophilic [9,10]. Tan et al., [3] for example, showed that the wettability of the stamp and the substrate are extremely important parameters for successful micro-contact printing. They showed that selectively modifying the wettability of a gold surface by stamping with thiols (–SH) and coating the remaining surface with thiols capped with different functional groups allowed the transfer of proteins in selected areas. Alternatively, functionalizing the stamp with a silane capped with –CF$_3$ decreased the wettability while –NH$_2$ capped groups

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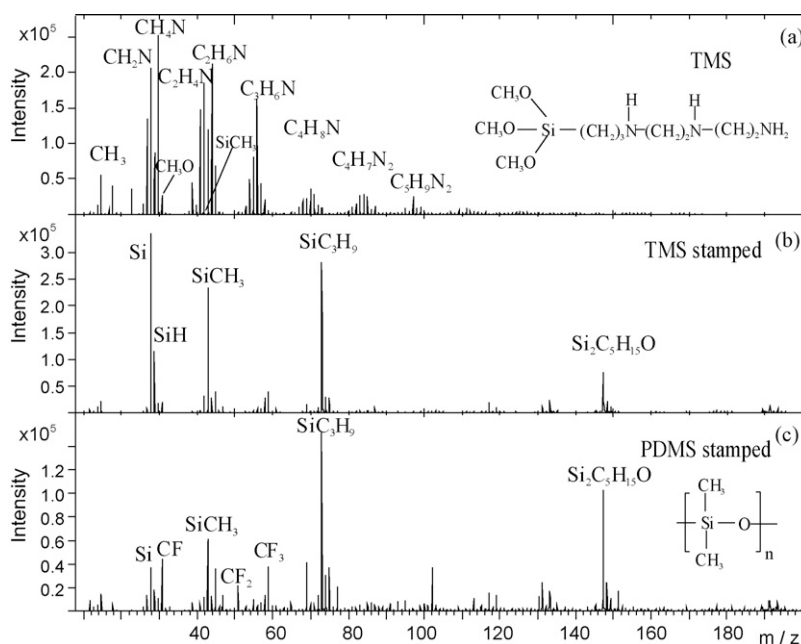 E-mail address: p.pigram@latrobe.edu.au (P.J. Pigram).

Fig. 1. Positive TOF-SIMS spectra for PTFE: (a) immersed in TMS; (b) stamped with TMS; and (c) stamped with blank PDMS.

increased the wettability. It is not clear, however, that these findings are generally applicable to other ink-substrate systems, in particular, organic inks and substrates of different surface chemistry and wettability.

The current study focuses on micro-contact printing of plasma-treated fluoropolymer (PTFE) surfaces with tri-methoxysilane N-[3-(trimethylsilyl)propyl]diethylene triamine (TMS); a silane incorporating active amine groups (see Fig. 1 for chemical structure). These amine groups were then coordinated with a palladium catalyst to allow the electroless deposition of copper [11]. Previous patterning techniques for metals focused on printing thiol masks [12] or palladium catalysts [13–15], which used water or ethanol as solvents. Micro-contact printing of silanes has been investigated by several groups but usually on glass or metal substrates [16,17]. Silanes bond to the surface through a hydroxyl group (Si–OH) and cross-polymerize to form a complete layer (not necessarily a monolayer). The solvent used in the current study (see Section 2) was dioxane which caused the silane to favor a surface hydrolysis over a solution hydrolysis reaction.

2. Experimental

Masters with large features (200 μm wide lines) were mechanically fabricated by cutting grooves in aluminum blocks with a silicon carbide disk saw. For producing PDMS stamps, Sylgard 184 silicone elastomer was mixed with a curing agent (Dow Corning, USA) at a ratio of 10:1 by weight. The mixture was then poured over a master and allowed to cure at room temperature for 3 days. This curing technique resulted in excessive amounts of silicone being transferred to the surface from these stamps. In the current method, the fluid was evacuated using a dessicator and a rotary pump which maintained the pressure at about 10^{-1} Torr for 20 min. This

allowed air bubbles in the mixture to be removed. The fluid was then poured over the master and subsequently evacuated for 10 min. This ensured that air trapped under the master and any remaining air bubbles were also removed. The final step was curing at 60 °C for 48 h. This over-curing ensured that most of the mobile silicone components were completely cross-linked before stamping.

Plasma treatment of stamps used a cylindrical glow discharge cell (Model PDC-32G, Harrick Scientific Corp., USA) and a plasma power of 18 W at a pressure of argon gas (99.999% purity, Linde) about 5×10^{-2} mbar for a period of 60 s.

The stamps were immersed in a solution of 4%, w/w TMS $(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2)$) in 1,4-dioxane both obtained from Aldrich, for 5 min and dried in a stream of nitrogen. The stamp was then brought into conformal contact with an Ar-PTFE surface for varying amounts of time and with varied amounts of pressure. The surface was analyzed using XPS and TOF-SIMS. Copper micro-patterns were grown as described previously [11,18].

XPS measurements were performed using an Axis Ultra spectrometer (Kratos Analytical Ltd., UK), equipped with a monochromatised X-ray source (Al Kα, $h\nu = 1486.6$ eV) operating at 150 W. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$ photoelectron peak at binding energy ($E_B = 83.98$ eV). Survey spectra were acquired for binding energies of 0–1100 eV, using a pass energy of 160 eV. The region spectra were acquired at a pass energy of 20 eV to obtain higher resolution spectra. The peaks were fitted with synthetic Gaussian–Lorentzian components using the Marquardt fitting procedure of CasaXPS and were quantified using the sensitivity factors for the Kratos instrument. The analysis area was 700 μm × 300 μm. Several spots were analyzed on each surface to investigate surface homogeneity and representative results are presented. TOF-SIMS analyses were performed using

a TOF-SIMS IV instrument (Ion-TOF GmbH, Germany) equipped with a reflectron analyzer, a Ga^+ ion gun (25 keV) and a pulsed electron flood source for charge neutralization. The primary pulsed ion beam current was 2.5 pA and the primary ion dose density was below the static SIMS limit of 10^{13} ions cm^{-2}. Both high mass resolution spectra (>7500 at $m/z = 29$) and high lateral resolution images (~1 μm) were recorded. For spectral acquisition, positive and negative ion mass spectra were acquired from a 100 μm × 100 μm area using a cycle time of 100 μs.

3. Results and discussion

X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were used to analyze the stamped surfaces. Table 1 presents the relative atomic concentration of the silicon and nitrogen species from the XPS results. Since both the ink and the stamp contained silicon species, it was difficult to extract the silicone component (PDMS stamp) from the deposited silane (ink) other than by calculating the nitrogen to silicon ratio (Table 1). For pure TMS, the N:Si ratio should be 3:1 (from the chemical structure in Fig. 1a) although the attenuation of the photoelectrons through the surface overlayer may alter this ratio. PTFE immersed in the inking solution has a N:Si ratio of 2.6. This ratio decreased for stamped surfaces due to the presence of contaminating silicones. For a room temperature cured PDMS stamp, the amount of silicones transferred during stamping was relatively high (N:Si = 0.3). A baked PDMS stamp, however, produced a much lower level of silicone (N:Si = 1). This demonstrates that curing the stamp at elevated temperatures reduces the amount of silicone transfer. Stamping with a blank, non-patterned, non-inked stamp indicated the amount of silicone transfer as approximately 2.5 at.%. The amount transferred varied from 0 to 3 at.%, depending on the amount of time the stamp was in contact with the PTFE surface and varied as much as 1 at.% between different analysis spots on the same surface. Generally, the amount of silicone transferred from a properly cured PDMS stamp was less than 1 at.%. This compares with the 6–10 at.% silicone transferred from untreated PDMS and 0.2–3.6 at.% silicone transferred from UV/ozone-treated PDMS stamps reported by Glasmaster et al., [6] and the 0.3–1.2 at.% detected randomly by Graham et al., [5] after their week long pretreatment of PDMS stamps.

There are two critical issues for successful micro-contact printing: the stamp material and the ink (including solvent). The stamp and ink must be compatible, as sufficient ink must be adsorbed by the stamp for transfer to the target surface. However, proper release of the ink onto a surface requires that the ink have a

higher affinity for the surface than for the stamp [7]. The high affinity of thiols for gold makes stamping relatively easy as it requires very little contact time between stamp and substrate and minimal stamp pre-treatment. However, for other systems such as proteins or water-based systems, the stamps are generally pre-treated to make the surface more hydrophilic and to allow some absorption of the ink. In the current study, the stamp must remain hydrophobic; in particular, silane—stamp bonding through oxygen-containing groups must be avoided. This issue was explored by testing the behavior of Ar plasma-treated PDMS stamps. Treated stamps used for blank (no ink) stamping tests performed well; no silicone was transferred, consistent with previous studies discussed above. However, such stamps do not transfer silane species effectively as the affinity between the silane and the stamp is almost as strong as that between the activated PTFE and the silane. Therefore, a hydrophobic PDMS stamp is preferable to transfer silane to the PTFE surface effectively and allow the desired silanol bonding process to occur at the surface.

TOF-SIMS spectra of stamped PTFE (Fig. 1c) and PTFE immersed in TMS (Fig. 1a) demonstrate the differences between the mass fragments from the PDMS and the silane. The major mass fragments are outlined in Table 2. The TOF-SIMS spectrum of PTFE immersed in TMS (Fig. 1a) contains a series of fragments, the major components of which are related to CH_2^+ and CH_2N^+ species. The silicone fragments, Si^+ ($m/z = 28$) and $SiCH_2^+$ $m/z = 42$), and oxygen fragments, CH_3O^+

Table 1
Relative percentage atomic concentrations from XPS spectra

PTFE sample conditions	Si	N	N:Si
Immersed in ink solution	4.7	12.3	2.6
Stamped with inked baked stamp	10.0	10.0	1.0
Stamped with inked stamp (RT cured)	14.3	4.5	0.3
Stamped with bare baked stamp	2.5		

Table 2
List of major positive ion fragments from TOF-SIMS spectra of PTFE immersed in TMS and PTFE stamped with unpatterned, non-inked PDMS

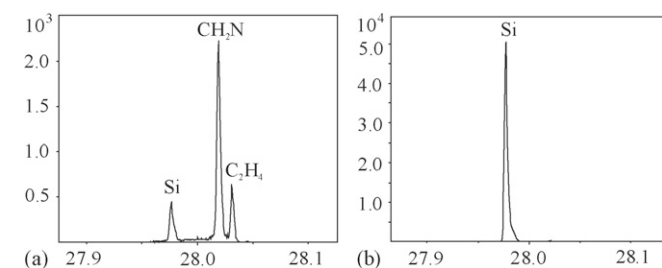| Major Peaks for TMS		Major Peaks for PDMS	
m/z	Ion fragment	m/z	Ion fragment
15	CH_3	15	CH_3
17	NH_3	28	Si
18	NH_4	30	SiH_2
27	C_2H_3	31	CF
28	CH_2N	42	$SiCH_2$
29	CH_3N	43	$SiCH_3$
30	CH_4N	50	CF_2
42	C_2H_4N	57	SiC_2H_5
44	C_2H_6N	69	CF_3
56	C_3H_6N	73	SiC_3H_9
70	C_4H_8N	147	$Si_2C_5H_{15}O$
83	$C_4H_7N_2$	207	$Si_3C_5H_{15}O_3$
97	$C_5H_9N_2$	221	$Si_3C_7H_{21}O_2$

Fig. 2. Positive TOF-SIMS spectra for PTFE: (a) immersed in TMS; and (b) stamped with blank PDMS showing the major components of the peak at $m/z = 28$.
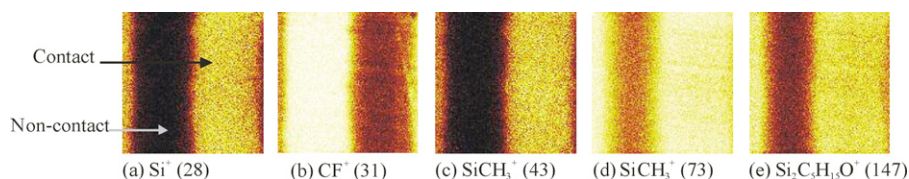
Fig. 3. TOF-SIMS images in positive ion mode for selected fragments for a blank stamped PTFE surface. The stamp was in contact with the PTFE surface at 200 μm wide lines separated by 200 μm wide spaces. Scan size is 500 μm × 500 μm. All images were acquired from the same area of the sample.

($m/z = 31$) are also present but at much smaller intensities as shown in Fig. 2. The mass peak at $m/z = 28$ in the TMS spectrum (shown in Fig. 2a) is a combination of Si^+, CH_2N and $C_2H_4^+$ with the largest component being CH_2N^+. By contrast the same region in the PDMS spectrum contains only the Si^+ mass peak with the CH_2N not visible. The major mass fragments for TMS are in the low mass region below 140 m/z. Polymerized TMS would contain Si–O–Si groups which would be clearly visible in the high mass region, hence it is clear that SAM of TMS are not highly polymerized. Stamped TMS layers are relatively thin, non-polymerized, self-assembled monolayers however, as is clear from Fig. 1b, higher mass fragments associated with silicone fragments are also present.

In addition to peaks at $m/z = 31$ (CF^+), 50 (CF_2^+) and 69 (CF_3^+) attributed to the fragments of PTFE, the blank stamped surface (Fig. 1c) is dominated by characteristic siloxane peaks at $m/z = 28$ (Si^+), 43 ($SiCH_3^+$), 73 ($SiC_3H_9^+$) and 147 ($Si_2C_5H_{15}O^+$) [19]. The most intense peaks in the PDMS spectrum are $m/z = 73$ and 147, the higher mass components. These peaks correspond to the degradation of the PDMS polymer chain and subsequent loss of methyl terminated and methyl-oxygen terminated groups. The spectrum (Fig. 1b) of stamped TMS also displays the silicone mass fragments but at slightly lower intensities and different intensity ratios, with the major peak appearing at $m/z = 28$. The nitrogen-containing mass fragments are also present albeit at lower intensities. The shape of the $m/z = 28$ region for the TMS stamped surface is similar to Fig. 2b however, as can be seen from Fig. 1, the intensity is higher for TMS stamped than for PDMS stamped surfaces. This increase is due to silicon components from TMS as well as from PDMS, which also contribute to an increase in the other major peaks at $m/z = 43$ and 73 (but not $m/z = 147$ which is entirely due to PDMS). Some reactions between the ink and the stamp may occur (both being siloxane polymers) prior to stamping a TMS layer and this may increase the amount of PDMS transfer. As TOF-SIMS is more sensitive to silicones than to nitrogen, the difference between the spectra of blank stamped and TMS stamped PTFE is not pronounced except in the low mass region and the relative intensity of the peaks.

TOF-SIMS images of PTFE stamped with a patterned (200 μm lines) PDMS stamp show silicon across the entire surface with the highest intensity localized around the contact regions (bright areas in Fig. 3). The non-contact region is identified from Fig. 3b by CF^+ ($m/z = 31$), a fragment from the underlying PTFE surface. The higher mass fragments of $SiC_3H_9^+$ ($m/z = 73$) (Fig. 3d) and $Si_2C_5H_{15}O^+$ ($m/z = 147$) (Fig. 3e), are more intense than the lower mass fragments Si^+ ($m/z = 28$) (Fig. 3a) and $SiCH_3^+$ ($m/z = 43$) (Fig. 3c), which is consistent with the spectra in Fig. 1. Since PDMS is formed from large siloxane polymer chains, the dominance of the higher m/z fragments over the lower m/z fragments is not unexpected. In particular, the mass fragment at $m/z = 73$ appears to cover almost the entire surface despite only the 200 μm lines being in contact with the PTFE. This could be due to low molecular weight components of the PDMS (those with more methyl terminated groups) being highly volatile [19]. The set of images in Fig. 3 demonstrate that silicone is transferred from blank stamps during the micro-contact printing process and raises the question of how might this contamination be distinguished from the TMS ink on stamped PTFE surfaces.

Fig. 4 shows TOF-SIMS images for the same set of m/z fragments from a TMS stamped surface. Silicone fragments are present over the whole surface but the lowest mass fragment at ($m/z = 28$) is most intense in the regions where the stamp was in contact with the surface as indicated by the bright central region in Fig. 4a. The non-contact region is again identified by CF^+ ($m/z = 31$) in Fig. 4b. The fragment in Fig. 4c includes $SiCH_3^+$ as well as C_2F^+ which contributes to the intensity in the non-contact areas, however it is clear there is additional intensity (as compared to Fig. 4b) in the central contact region due to $SiCH_3^+$. The fragments for higher values of m/z (Fig. 4d and e) are present in the non-contact regions indicating a transfer of silicone to these areas. In particular, the most intense stripes are at the edge of the contact region where imperfections in the stamp edges caused large amounts of silicones (high mass fragments) to be transferred. This separation allows a distinction to be made between PDMS, which is dominated by $SiC_3H_9^+$ ($m/z = 73$) and $Si_2C_5H_{15}O^+$ ($m/z = 147$) (high m/z
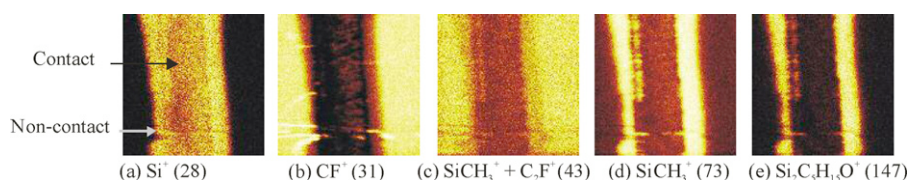

Fig. 4. TOF-SIMS images in positive ion mode for selected fragments characteristic of TMS-patterned PTFE surface using a PDMS stamp. The stamp was in contact with the PTFE surface at 200 μm wide lines separated by 200 μm wide spaces. Scan size is 500 μm × 500 μm. All images were acquired from the same area of the sample.

fragments), and TMS, which is dominated by Si^+ ($m/z = 28$) and $SiCH_3^+$ ($m/z = 43$) (low m/z fragments). This reasoning is also supported by the different intensity ratios of the $SiC_3H_9^+$ peak to the Si^+ peak in Fig. 1a and b, respectively. Hence, the major difference is not in the absence of silicone peaks but in the relative intensity of these peaks. Silicone transfer occurs across the whole surface but silane transfer is limited to the contact positions.

4. Conclusions

TOF-SIMS is more sensitive to silicones than XPS and inherently more surface sensitive as well. Therefore, it is not surprising to detect PDMS fragments from a stamped surface; in fact, it would seem that most stamped surfaces will exhibit some siloxane species. It is also apparent from the results from this study (and others), that removing these silicone components completely is not possible. Most researchers do not have routine access to the surface analytical techniques required to monitor silicone contamination and it is likely that many published results have inherent contamination problems. Still, from the large body of literature devoted to micro-contact printing using PDMS stamps, it seems that silicone contamination does not affect the final outcome of patterned surfaces. However, as researchers push the limits of the micropatterning technique into the nanoscale region this assumption may no longer apply.

Acknowledgments

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