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Article

Effect of Surface Free Energy on PDMS Transfer in Microcontact Printing and Its Application to ToF-SIMS to Probe Surface Energies

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Although PDMS transfer during microcontact printing (μCP) has been observed in previous reports, which generally focused on only one or a few different substrates, in this work we investigate the extent of PDMS transfer onto a series of surfaces with a wide range of hydrophobicities using an uninked, unpatterned PDMS stamp. These surfaces include clean silicon, clean titanium, clean gold, "dirty" silicon, polystyrene, Teflon, surfaces modified with PEG, amino, dodecyl, and hexadecyl monolayers, and also two loose molecular materials. The PDMS transferred onto planar surfaces is, in general, easily detected by wetting and spectroscopic ellipsometry. More importantly, it is detected by time-of-flight secondary ion mass spectrometry (ToF-SIMS) because of the sensitivity of this technique to PDMS. The effect of surface free energy on PDMS transfer in microcontact printing is investigated, and the relationship between the amount of PDMS in ToF-SIMS spectra and the surface tensions of initial surfaces is revealed. We show that PDMS transfer can be applied as a probe of surface free energies using ToF-SIMS, where PDMS preferentially transfers onto more hydrophilic surface features during stamping, with little being transferred onto very hydrophobic surface features. Multivariate curve resolution (MCR) analysis of the ToF-SIMS image data further confirms and clarifies these results. Our data lend themselves to the hypothesis that it is the free energy of the surface that plays a major role in determining the degree of PDMS transfer during μCP.

Introduction

Microcontact printing (μCP) is a well-recognized and important tool for the selective patterning of surfaces on the microscale and nanoscale with a wide variety of adsorbates.[1,2] In μCP, a patterned elastomeric stamp, usually polydimethylsiloxane (PDMS), is "inked" with a molecule/species of interest and then brought into contact with a substrate. Ideally, transfer of the ink takes place only at the raised points of the stamp that make contact with the substrate. A current and important topic in μCP is the transfer of low-molecular-weight oligomers of PDMS that often accompany ink transfer.[3,4] PDMS is a rather common contaminant of many surfaces and materials, and ToF-SIMS, even with the older Ga^+ guns, is exquisitely sensitive to it, showing strong characteristic signals.

A series of reports in the literature leave no doubt regarding the transfer of PDMS oligomers during μCP. In 1999, Böhm and co-workers used X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy to show that a significant amount of PDMS contamination occurs during μCP of dodecanethiol on gold, where their printing was done at fairly high pressures. The only precleaning of their stamps was a rinse in ethanol.[5] In 2000, Yang and co-workers observed PDMS transfer in microcontact printing on functionalized poly(ethylene terephthalate). In a control experiment, fluorescence microscopy of a microcontact-printed surface suggested that PDMS transfer enhanced streptavidin chemisorption. The presence of PDMS after μCP was confirmed by imaging ToF-SIMS. Transferred PDMS could be partially removed by sonicating in ethanol.[6] In 2002, Graham and co-workers published a detailed study of the transfer of PDMS onto gold surfaces during microcontact printing with dodecanethiol. Their study included an exhaustive cleaning of the stamps that took approximately 1 week (a series of extractions consisting of soaking or sonicating in different solvents). After this cleaning procedure and a final blotting, PDMS could be detected only at the detection limit of XPS (ca. 1%) in a subset of their samples. However, a principal components analysis of ToF-SIMS data from a series of surfaces prepared with increasing concentrations of a dodecanethiol ink indicated that PDMS transfer consistently occurred during μCP but decreased with increasing thiol concentration. Their work is a statement of the sensitivity of ToF-SIMS for PDMS and its importance as one of the tools that provide conclusive identification of it.[7] A year later, Glasmästar and co-workers introduced a UV/ozone treatment of PDMS stamps as a method for reducing PDMS transfer during μCP. This procedure only took a few minutes and had the advantage (or disadvantage, depending on the need) of yielding a hydrophilic stamp. PDMS transfer during μCP was demonstrated using Milli-Q water as the ink.[8]

In 2004, Zhou and co-workers studied the conditions for μCP of various oligo(ethyleneglycol)-containing thiols using

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A

oxygen-plasma-treated stamps.[9] In their work, infrared reflection—absorption spectroscopy clearly showed PDMS transfer to gold substrates during μCP and suggested that (i) the PDMS is located at the top of the monolayer and (ii) it is easily removed by a short period of sonication in ethanol. A reduction in the water contact angle to a level similar to that obtained with solution-prepared monolayers accompanied the PDMS extraction of printed surfaces with solvents. Vickerman and Briggs have also reported that PDMS contamination of surfaces in general can be removed by sonication with hexane, acetone, and methanol.[10] In 2005, Langowski and Uhrich studied different oxygen plasma treatments of PDMS stamps to reduce PDMS transfer during μCP to oxidized PMMA, where the "ink" was deionized water. After plasma treatment, X-ray photoelectron spectroscopy showed a large increase in the oxygen content of the stamps, a large decrease in the carbon content, and a substantial decrease in PDMS transfer under all plasma treatment conditions studied.[11] In related work, Felmet and co-workers reported nanotransfer printing of copper lines onto dithiol-modified GaAs. The copper lines were always nonconductive and were found to be filled with PDMS, unless the stamp was first leached with toluene, which reduced PDMS contamination.[12] Bhattacharya and co-workers have also studied plasma oxidation of PDMS for use in microfabrication.[13]

Tingey and co-workers attributed, at least in part, the non-specific transfer of material observed by ellipsometry during affinity μCP to PDMS from the stamp.[14] Thomson and co-workers similarly hypothesized that material observed by SEM after μCP may have been due to impurities from the PDMS stamp.[15] Perl and co-workers studied a new dendromer-based ink for positive microcontact printing on gold. They reported water contact angles of surfaces made by printing with their inks ($79 \pm 2°$) that were ca. 20° higher than the corresponding surfaces prepared by solution assembly ($59 \pm 4°$). They attributed this difference in wetting to PDMS transfer from the stamp.[16] Zhao and co-workers used wetting to show the transfer of PDMS oligomers from a PDMS mold in replica molding of polyimide.[17]

As noted above, the presence of low-molecular-weight oligomers of PDMS transferred during the μCP of proteins often enhances protein transfer from the stamp. This effect also appears to be operative for DNA (vide infra). However, Foley et al. studied antibody binding to a protein antigen that had been deposited on gold using μCP. They used surface plasmon resonance and XPS to show significant silicone (PDMS) oligomer transfer, noting that less protein was transferred by μCP than the amount of protein adsorbed from solution.[18] In contrast, Ross and co-workers studied μCP of bovine serum albumin (BSA) on polymerized lipid bilayers and glass. In their work, the amount of protein transferred by μCP was greater than that obtained by nonspecific adsorption from solution. In addition, much more protein transfer occurred from hydrophobic (unoxidized) PDMS stamps than from (air) plasma-oxidized stamps. Low-molecular-weight oligomers of PDMS were transferred to surfaces from uninked stamps, and the adsorbed PDMS was found to increase subsequent BSA adsorption from solution. Their PDMS stamps were cured at fairly high temperature compared to that of other researchers: 100 °C for 2 h.[19] Thibault and co-workers found that DNA transfer, along with its subsequent hybridization, was much more effective for stamps that had not undergone Soxhlet extraction (vide infra) (i.e., the transfer of PDMS oligomers during μCP-enhanced DNA adsorption[20]).

There is some question as to the efficiency of the different extraction methods that have been employed to remove unbound PDMS from stamps. In general, most of the methods that have been described, such as solvent extraction (soaking), UV or plasma treatment, or long cure times, are not completely effective in eliminating the transfer of low-molecular-weight PDMS oligomers during μCP.[18] For example, Hale and co-workers showed that baking the PDMS significantly reduced, but by no means eliminated, the amount of PDMS transfer in μCP of an amino silane, compared to PDMS transfer from the unbaked stamp.[21] However, of all the methods investigated, Soxhlet extraction may be the most promising. Although Sharpe and co-workers,[22] who may have been the first to apply this technique to clean PDMS stamps, reported that extraction did not diminish PDMS transfer in μCP. Tan and co-workers showed that Soxhlet extraction of PDMS stamps prevented the transfer of PDMS oligomers during affinity μCP of DNA,[23] and Thibault and co-workers[20] showed that Soxhlet extraction of PDMS stamps would similarly eliminate the transfer of low-molecular-weight oligomers of PDMS. Thus, there is at least some suggestion that Soxhlet extraction may be the most efficient extraction method contemplated to date.

PDMS transfer from uninked (and unextracted) stamps has also been employed as a useful surface-patterning tool. In 2004, Wang and co-workers modified polymer surfaces by stamping with uninked PDMS stamps. PDMS transfer was confirmed by atomic force microscopy (AFM) and infrared spectroscopy and the residual PDMS could be used to direct subsequent polymer deposition in spin- or dip-coating.[24] Briseno and co-workers employed the same technique to transfer PDMS as a resist for dip coating organic semiconductors. PDMS transfer was confirmed by quartz crystal microbalance (QCM), Fourier transform infrared spectroscopy (FTIR), XPS, wetting, and mass spectrometry. No effective resist layer was deposited when solvent-extracted (soaked) PDMS stamps were employed.[25] Åsberg and co-workers also used the transfer of low-molecular-weight PDMS oligomers from patterned, uninked, PDMS stamps as a method for creating patterns with hydrophobic and hydrophilic areas and then observed selective adsorption to the PDMS of biomolecules and biomolecule conjugates.[26] Wigenius and co-workers then used imaging ellipsometry and AFM to study PDMS transfer from uninked stamps to SiO_2- and $SiCl_2(CH_3)_2$-treated substrates.[27] They found that the thickness of the transferred material

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178 increased with the contact time between the stamp and the
179 substrate and that the resulting patterns of PDMS were unstable
180 with time, forming submicrometer droplets on the surfaces.
181 Similar submicrometer features appear to be present in Sharpe's
182 AFM images and are attributed to contamination from the
183 stamp.[22]

184 Sharpe and co-workers recently studied PDMS contamination
185 by AFM, XPS, and FTIR during μCP on gold for both a
186 hydrophilic (16-mercaptohexadecanoic acid, MHDA) and a
187 hydrophobic ink (*n*-octadecanethiol, ODT).[22] They noted that
188 significant PDMS contamination was observed when MHDA
189 was printed but little or no contamination was observed if ODT
190 was printed. This same effect was observed whether uninked
191 stamps or stamps inked with MHDA or ODT were brought into
192 contact with preformed MHDA or ODT monolayers, respec-
193 tively. They proposed that hydrophilic contaminants are ad-
194 sorbed from PDMS stamps onto surfaces during μCP, which
195 have a high affinity for hydrophilic inks and surfaces.[22] That is,
196 they interpreted their results in terms of hydrophilic inks promot-
197 ing the adsorption of hydrophilic species. We will comment on
198 their hypothesis in the Discussion of this article.

199 All of this earlier work sets the stage for our present study on
200 PDMS transfer onto a variety of different surfaces. Indeed, to the
201 best of our knowledge, this article represents the first systematic
202 study of PDMS transfer from uninked and unextracted stamps to
203 a series of surfaces that exhibit a wide range of hydrophobicities.
204 Furthermore, it appears to be the first detailed study that
205 articulates that the surface wetting (free energy) of the substrate
206 plays a critical role in determining the extent of PDMS oligomer
207 transfer during μCP. We then use this phenomenon to demon-
208 strate that PDMS oligomer transfer in μCP can be used in
209 conjunction with ToF-SIMS as an effective tool for probing
210 surface free energies on the micrometer scale, where PDMS
211 oligomer transfer occurs preferentially to hydrophilic surfaces
212 or surface features over more hydrophobic regions (Scheme 1). Of
213 course, we acknowledge that there may very well be other factors,
214 in different situations, that may influence PDMS transfer during
215 μCP. Such factors may include the contact time of the stamp with
216 the substrate, the pressure on the stamp, the concentration and
217 chemical nature of the ink and its solvent, and the curing,
218 extraction, chemistry, and/or pretreatment of the stamp. Never-
219 theless, we affirm in this work that a dominant factor in this
220 process appears to be the surface free energy of the substrate.

221 Because PDMS contamination is a common problem in
222 materials analysis by ToF-SIMS and the deliberate introduction
223 of PDMS into a SIMS system may seem to be a fairly strange
224 proposition to many practitioners of this technique, we emphasize
225 that the few angstroms or nanometers of PDMS that adsorb to
226 our surfaces in this study have not caused any noticeable
227 contamination of our ToF-SIMS instrument. We also wish to
228 emphasize that our work is not a report of a new contrast agent
229 for SIMS, which might improve the ion yields from our gallium
230 liquid metal ion source. Rather, a material's adsorption of PDMS
231 oligomers (or lack thereof) from planar PDMS stamps is shown
232 to be a useful surface probe that can reveal the hydrophobicity or
233 hydrophilicity of surface features by ToF-SIMS, providing at
234 least a relative measure of the wetting properties of microscopic
235 surface features. Hence, the application of this technique should
236 not be dependent on any particularly SIMS primary ion source.

Experimental Section

237

238 **Solvents.** Toluene and chloroform were spectral grade
239 and purchased from Aldrich. Buckminsterfullerene (99.5%)
240 was obtained from SES Research (Houston, TX). Tri-

Scheme 1. Illustration of the PDMS Contrast Stamping Method[a]
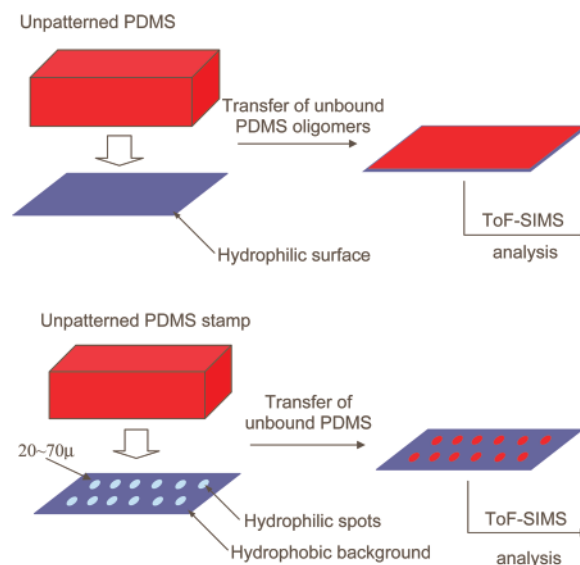
[a] A planar PDMS stamp is pressed against a surface. Transfer of
unbound PDMS oligomers in the stamp occurs preferentially at hydro-
philic regions on the surface, over more hydrophobic regions.

241 hexadecyloxybenzaldehyde (THOB) was obtained from the
242 Advanced Materials Laboratory, National Institute for
243 Materials Science (Namiki, Tsukuba, Ibaraki, Japan), and was
244 used as received. Sylgard 184 silicone elastomer and curing
245 reagent were purchased from the Dow Corning Cor-
246 poration. 2-[Methoxy(polyethylenoxy)propyl] trimethoxysilane
247 ((CH$_3$O)$_3$Si(CH$_2$)$_3$(OCH$_2$CH$_2$)$_{6-9}$OCH$_3$, ≥90%, M_w 460−590,
248 6−9 PEG units) was obtained from Gelest (Tullytown,
249 PA). Trichloro(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)
250 silane (CF$_3$(CF$_2$)$_5$CH$_2$CH$_2$SiCl$_3$, ≥97%) was from Fluka.
251 1-Hexadecene (∼99%), 1-dodecene (≥99%), and polystyrene
252 (average M_w ∼192 000) were obtained from Aldrich. Fluoro Pcl
253 PFC M1604V was obtained from Cytonix Corporation.

254 **Solid Surfaces.** Silicon wafers (100) were obtained from
255 Montco Silicon Technologies, Inc. Titanium and gold films on
256 silicon wafers were obtained by electron beam evaporation at
257 BYU. These surfaces were cleaned in a Harrick plasma cleaner
258 (model number PDC-32G, power 18 W) with air plasma prior to
259 stamping. "Dirty" silicon wafers are silicon surfaces that were
260 used as received from the manufacturer, without any surface
261 cleaning or rinsing.

262 **Thin Film Preparation.** Buckminsterfullerene (C$_{60}$, 8.6 mg)
263 was added to 3.0 mL of toluene to produce a saturated sol-
264 ution, where the theoretical solubility of C60 in toluene is
265 2.8−3.0 mg/mL.[28,29] In practice, most of the C$_{60}$ dissolved,
266 and the supernatant from this solution was used. Trihexadecy-
267 loxybenzaldehyde (THOB) was dissolved in chloroform
268 at a concentration of 0.5% (w/w). These solutions were placed
269 dropwise onto clean silicon shards, and the solvents
270 were allowed to evaporate, leaving thin molecular films of
271 these compounds. THOB thin films were also obtained on
272 silicon surfaces by spinning this solution. Polystyrene (average
273 M_w ∼192 000) was dissolved in toluene at a concentration of
274 0.5% (w/w). Polystyrene thin films were obtained by spinning
275 this solution. To create a hydrophobic Teflon-like film (the
276 "Teflon surface"), a silicon wafer was spin coated with Fluoro
277 Pcl PFC M1604V (Cytonix Corporation). After being
278 spun, these wafers were cured on a hot plate at 90 °C for 5 min
279 and then at 180 °C for 12 min.

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Monolayer Preparation. Perfluoro monolayer surfaces were made through the chemisorption of trichloro(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane. Plasma-cleaned silicon surfaces were placed in a desiccator and exposed to the vapor of this fluorinated silane overnight. The surfaces were then cured at 80 °C for an hour. 3-Aminopropyltriethoxysilane (APTES) surfaces were made by this same procedure using APTES. Polyethylene glycol (PEG) monolayer surfaces were made from $(CH_3O)_3Si(CH_2)_3(OCH_2CH_2)_{6-9}OCH_3$.[30] Plasma-cleaned silicon surfaces were immersed in a 4 to 5 mM solution of this PEG silane in toluene with 0.8 mL/L HCl(conc) for 18 h at room temperature. The wafers were then washed with toluene, ethanol, and water. Hexadecyl and dodecyl monolayer surfaces were made from neat 1-hexadecene and 1-dodecene, respectively. The surfaces were hydrogen terminated with HF and then immersed in degassed 1-hexadecene or 1-dodecene at 150 °C for 1 h under N_2. No particular attempt was made in this synthesis to produce surfaces with extremely high water contact angles, and the water contact angles observed on these surfaces were in the desired range for this particular study.

Hexadecyl and Dodecyl Monolayer Preparation (for UV Patterning). A commercially available silicon wafer with a low electrical resistance value was cleaved and then sonicated with acetone, dichloromethane, ethanol, and DI water in that order. Silicon shards were then photocleaned with a vacuum UV light. Photocleaned silicon was placed in a Teflon container, and then a sufficient quantity of 40% (by vol) NH_4F (used in commercial semiconductor processing) was added to the container. After 15 min, the sample was removed and then washed immediately with DI water. The H-terminated sample was placed in a 10 vol % solution of 1-hexadecene or 1-dodecene in mesitylene, bubbled with Ar for several hours, and finally heated for at least 12 h at the boiling temperature of mesitylene.

Surface Patterning with the Microlens Array. A microlens array (MLA)[30,31] with 100 μm spacing between microlenses (SUSS MicroOptics, Neuchatel, Switzerland) was placed approximately 200 μm over the PEG, perfluoro, APTES, or hexadecyl monolayer-coated silicon oxide substrates. A single ca. 4 ns pulse of 15 mJ 532 nm laser light (Coherent Infinity Nd: YAG laser) was then shot through this optical element to pattern the surface. The surface was not cleaned or rinsed in any way after MLA patterning.

Surface Patterning with UV Light. The surfaces terminated with hexadecyl and dodecyl monolayers were micropatterned by exposure to vacuum UV light generated from an excimer lamp (Ushio Inc., UER20-172V; $\lambda = 172$ nm and 10 mW/cm^2)[32,33] through a photomask in contact with their surfaces for 30 min at a reduced pressure of 10 Pa. A 10-mm-thick quartz glass plate (Asahi Glass, synthetic silica glass AQX for Xe$_2$ 172 nm excimer lamps) served as a top weight on the photomask so as to obtain complete contact between the mask and the sample surface. The transparency of the photomask and the quartz plate at 172 nm was about 93 and 90%, respectively. The total light intensity at the sample surface was estimated to be 8.4 mW/cm^2. The dose was about 15.1 J/cm^2.

PDMS Stamp Preparation. Stamps were fabricated from Sylgard 184 silicone elastomer (Dow Corning Corp.) mixed with curing agent in a 10:1 ratio. The mixture was placed in a flat-bottomed Petri dish and then in a vacuum desiccator for 1 h to remove bubbles from the elastomer. The elastomer was cured for 2 h at 80 °C. After the stamp had cooled, the PDMS was carefully removed from the Petri dish. Finally, the round stamp was cut into several pieces. All results reported herein were obtained using freshly made PDMS stamps.

Surface Stamping. Silicon, titanium, and gold surfaces and the silicon surfaces that were modified with various monolayers were contacted with the PDMS stamp for 2 s under light manual pressure.

Surface Characterization. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed with an ION-TOF ToF-SIMS IV instrument using monoisotopic 25 keV $^{69}Ga^+$ ions. ToF-SIMS spectra were collected for 100 s. ToF-SIMS images were collected after 150 scans at 2 shots/pixel. Raw data files of ToF-SIMS images were collected and saved for MCR. Advancing water contact angle measurements were obtained with a Ramé-Hart model 100-00 contact angle goniometer. An advancing contact angle was measured when the sessile drop had the maximum volume allowable for the liquid−solid interfacial area and just moved across the surface. The contact angles on both sides of the drop were measured and averaged. To ensure reproducibility, at least three measurements were carried out on each solid surface. Spectroscopic ellipsometry was performed with an M-2000 instrument from the J. A. Woollam Co. (Lincoln, NE). The wavelength range of this instrument is ca. 200−1000 nm.

Surface Tension Calculations. Young's equation ($\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl}$) describes the thermodynamic equilibrium of the three surface tensions related to a droplet of liquid on a surface: γ_{sv}, γ_{sl}, and γ_{lv}, where the subscripts sv, sl, and lv refer to the solid−vapor, solid−liquid, and liquid−vapor interfaces, respectively. Only two of the parameters in Young's equation (γ_{lv} and θ) are easily measured or obtained, which leaves one equation and two unknowns (γ_{sv} and γ_{sl}). To more easily determine solid−vapor surface tensions (γ_{sv}), an equation of state of interfacial tensions[34,35] has been developed:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}}e^{-\beta(\gamma_{lv} - \gamma_{sv})^2} \tag{1}$$

When this equation is combined with Young's equation, the following equation[34−36] is obtained:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}}e^{-\beta(\gamma_{lv} - \gamma_{sv})^2} \tag{2}$$

Hence, if γ_{lv}, θ, and empirically derived parameter β are known, then γ_{sv} is also known. γ_{sv} was determined using a short Matlab program that we wrote employing values of 0.0001247 (mJ/m^2)$^{-2}$ for β and 72.8 mJ/m^2 for γ_{lv} of water.[34,35] Note that this equation sets γ_{lv} equal to γ_{sv} when $\theta = 0$ (when a surface is wet by water), which may or may not be correct for a given surface.

Multivariate Statistical Analysis of the ToF-SIMS Data. The multivariate curve resolution (MCR) algorithm in the Automated eXpert Spectral Image Analysis (AXSIA) tool kit developed at Sandia National Laboratories[37,38] was used to perform multivariate statistical analysis of the ToF-SIMS raw data files. For MCR analysis, the mass range of 0 to 300 amu was binned to 1 amu, and the data were properly scaled to account for Poisson statistics (noise in most ToF-SIMS studies is approximately Poisson-distributed), which affords maximum discrimination of chemical information from noise and allows small spectral features to be detected that would otherwise be overlooked.[39] MCR analysis required about 3 s of computational time on a Dell D400 Lattitude computer with a

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397 1700 MHz processor and 1.046 GB of RAM. The advantages of
398 AXSIA have been summarized elsewhere.[40]

Results

400 **Effect of Surface Free Energy on PDMS Transfer.** We
401 begin our study by analyzing two molecular surfaces that were
402 prepared by depositing small amounts of two different com-
403 pounds from solution: buckminsterfullerene (C_{60}) and trihex-
404 adecyloxybenzaldehyde (THOB) (Scheme 2). Figure 1 shows the
405 ToF-SIMS spectra of a thin film of C_{60} before and after
406 stamping with an unlinked, unpatterned PDMS stamp. Whereas
407 C_{60} is a rather hydrophobic material, it is not as hydrophobic
408 as PDMS, which in fact appears to facilitate PDMS transfer.
409 Indeed, the obvious peaks at m/z 73 ($CH_3Si^+(CH_3)_2$), 147
410 ($CH_3Si(CH_3)_2OSi^+(CH_3)_2$), 207 (see Scheme 2 for structure),
411 and 221 ($CH_3Si(CH_3)_2OSi(CH_3)_2OSi^+(CH_3)_2$) make it clear
412 that a measurable quantity of PDMS has transferred to this
413 surface after stamping. This same technique was then applied
414 to a thin film of THOB, but as shown in Figure 2, no PDMS
415 transfer appears to take place. Indeed, the long alkyl chains of
416 this molecule would be expected to align themselves perpendi-
417 cular to the surface to create a very low free-energy material.
418 FTIR was performed on THOB (in KBr), which showed asym-
419 metric ($\nu_a(CH_2)$) and symmetric ($\nu_s(CH_2)$) methylene stretches
420 of 2916.8 and 2848.8 cm^{-1}, respectively. These values are
421 consistent with a high degree of ordering (all-trans) of the alkyl
422 chains in this compound. When this type of ordering of alkyl
423 chains appears in monolayers, it generally accompanies
424 high advancing water contact angles (110° or greater),[41−43]
425 which appear to be in the range in which PDMS transfer would
426 not be expected to occur. This same result (no PDMS transfer
427 during stamping) was obtained whether the THOB film
428 was relatively thick (deposited dropwise) or thin (deposited by
429 spin coating).
430 In addition to ToF-SIMS, two important surface analytical
431 methods for probing surface thicknesses and free energies are
432 optical ellipsometry and contact angle goniometry. Unfortu-
433 nately, these techniques could not be applied to thin films of C_{60}
434 and THOB. The unbound molecules in these films were moved
435 by water droplets in contact angle measurements, giving un-
436 stable results, and the films were too rough for optical ellipso-
437 metry. Therefore, to study the transfer of PDMS during μCP
438 with greater thoroughness and at a more fundamental level,
439 a series of planar surfaces were stamped that did not contain
440 loose molecular material and that could be better probed with
441 surface analytical techniques. These surfaces ranged from
442 extremely hydrophilic to very hydrophobic and included clean
443 silicon, clean titanium, clean gold, "dirty" silicon, polystyrene,
444 Teflon, and surfaces modified with PEG, amino, dodecyl,
445 hexadecyl, and perfluoro monolayers. Representative ToF-
446 SIMS spectra from these surfaces after stamping are shown in
447 Figure 1 of the Supporting Information. In particular, on
448 two very hydrophilic surfaces (clean Ti and clean gold) stamped
449 with PDMS, the m/z 73 and 147 ions, which are characteristic
450 of PDMS, are the dominant peaks in the spectra. For the
451 APTES and PEG surfaces, which are still rather hydrophilic,

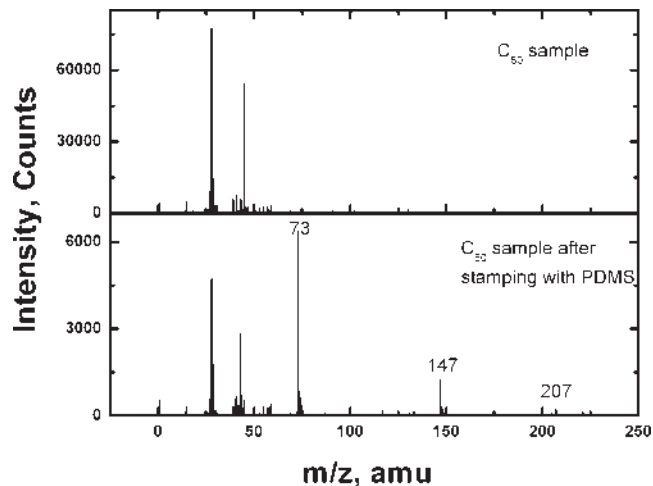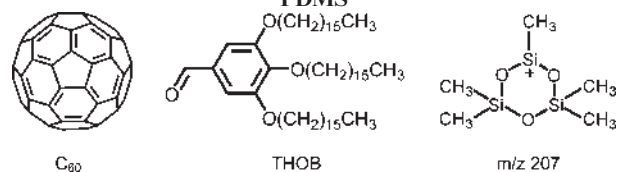**Scheme 2. Structures of C_{60} and THOB and the m/z 207 Peak from PDMS**

Figure 1. Positive ion ToF-SIMS spectra of a C_{60} film before and after stamping with PDMS.
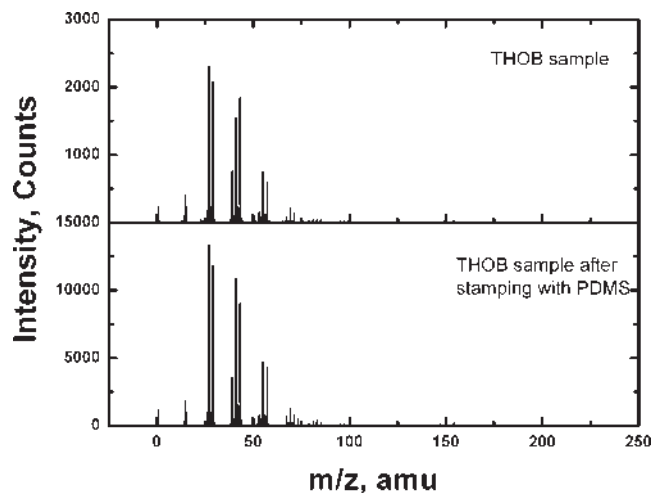
Figure 2. Positive ion ToF-SIMS spectra of a THOB film before and after stamping with PDMS.

452 these two ions from PDMS remain significant. For our hexade-
453 cyl monolayer on silicon and again for polystyrene, which
454 are more hydrophobic, the fraction of the peak area due to
455 these ions from PDMS has decreased. Finally, for the perfluori-
456 nated materials, which are the most hydrophobic in our
457 study, signals due to PDMS in the ToF-SIMS spectra are
458 scarcely discernible.
459 More quantitative results from ToF-SIMS, contact angle
460 goniometry, and spectroscopic ellipsometry before and after
461 stamping with unpatterned stamps are shown in Table 1. It is
462 clear from these data that the largest changes in water contact
463 angles after stamping occur with the surfaces that had the
464 smallest water contact angles to begin with (i.e., that were most
465 hydrophilic). The same trend is observed in the changes in
466 ellipsometric thicknesses: the largest changes in thickness after

(40) Smentkowski, V. S.; Ostrowski, S. G.; Kollmer, F.; Schnieders, A.; Keenan, M. R.; Ohlhausen, J. A.; Kotula, P. G. *Surf. Interface Anal.* **2008**, *40*, 1176–1182.
(41) Linford, M. R.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1993**, *115*, 12631–12632.
(42) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145–3155.
(43) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.

E

Table 1. Physical Properties of Various Surfaces before and after Stamping

	before stamping		after stamping					
surface	$\theta_a(H_2O)_{init}$ (deg)	γ_{sv} (mJ/m^2)	$\theta_a(H_2O)_{stamped}$ (deg)	γ_{sv} (mJ/m^2)	$\Delta\theta_a(H_2O)_{stamped}$ (deg)	$\Delta\gamma_{sv}$	$\Delta t_{stamped}$ (Å)	PDMS peaks (%)
clean Si/SiO$_2$	< 5	72.5	28.2 ± 1.2	65.3	23.2 ± 1.2	−7.2	10.1 ± 2.7	33.4 ± 1.3
clean Ti/TiO$_2$	< 5	72.5	28.2 ± 1.8	65.3	28.2 ± 1.8	−7.2	10.0 ± 3.3	36.1 ± 0.8
clean Au	< 5	72.5	33.2 ± 3.0	62.9	28.2 ± 3.0	−9.6	14.1 ± 4.0	48.0 ± 13.6
dirty Si/SiO$_2$	27.6 ± 1.7	65.6	33.3 ± 1.8	62.9	5.7 ± 2.5	−2.7	9.4 ± 2.9	31.5 ± 0.2
SiO$_2$/PEG monolayer	30.6 ± 0.8	64.2	38.9 ± 0.7	60.0	8.3 ± 1.1	−4.2	5.7 ± 1.0	36.6 ± 0.7
SiO$_2$/APTES monolayer	52.8 ± 2.7	52.1	61.6 ± 1.7	46.9	8.8 ± 3.2	−5.2	8.1 ± 1.7	39.1 ± 7.7
SiO$_2$/polystyrene	90.8 ± 1.0	28.7	94.6 ± 3.5	26.4	3.8 ± 3.6	−2.3	4.7 ± 0.5	20.7 ± 6.6
PDMS stamp	89.0 ± 1.4	29.8					^{a}	
Si/dodecyl monolayer	97.1 ± 4.0	24.8	96.3 ± 3.4	25.3	−0.8 ± 4.2	0.5	5.5 ± 0.8	24.3 ± 0.4
Si/hexadecyl monolayer	98.2 ± 2.6	24.1	97.3 ± 2.4	24.7	−0.9 ± 3.5	0.6	5.3 ± 1.7	21.0 ± 2.3
SiO$_2$/perfluoro monolayer	107.7 ± 2.1	18.4	107.3 ± 0.8	18.7	−0.4 ± 2.3	0.3	1.7 ± 1.9	2.4 ± 0.2
Teflon surface	118.1 ± 0.8	12.6	117.2 ± 0.9	13.1	−0.9 ± 1.2	0.5	0.3 ± 1.6	0.4 ± 0.4

^{a} Ellipsometry could not be performed on this surface. ^{b} Surface tension γ_{sv} of different surfaces before and after stamping calculated from mean advancing water contact angles (γ_{lv} = 72.8 mJ/m2 and β = 0.0001247 (mJ/m^2)$^{-2}$).

stamping occur for the samples that initially had the highest surface free energies. Likewise, the hydrophilic surfaces had the largest fraction of PDMS peaks in their ToF-SIMS spectra after stamping. Because surfaces with similar initial water contact angles responded similarly during stamping, the results from similar surfaces are grouped in the discussion of results below.

Air-plasma-cleaned silicon dioxide (Si/SiO$_2$), e-beam-evaporated titanium (Ti/TiO$_2$), and e-beam-evaporated gold were all wet with water (they had water contact angles of less than 5°) just prior to stamping. The extremely low water contact angles of these surfaces are indicative of their high surface free energies. After stamping, the water contact angles of these surfaces increased substantially, and their ellipsometric thicknesses increased by ca. 10 Å. The presence of PDMS on these surfaces is confirmed by the highly characteristic m/z 73, 147, 207, and 221 ions in their ToF-SIMS spectra. These peaks were not present in the spectra prior to stamping. The percentage of main PDMS peaks (m/z 73 and 147) in the total spectral area from 0 to 150 amu varies from 32 to 47% for the clean silicon, titanium, and gold surfaces after stamping. All of these results are consistent with significant PDMS transfer that lowers the surface free energies by covering high free-energy surfaces with a lower free-energy molecule (PDMS).

Three surfaces with somewhat higher advancing water contact angles than this initial set were also studied: "dirty" silicon/silicon dioxide, which is silicon that is contaminated with adventitious hydrocarbons (used-as-received silicon), a PEG monolayer on Si/SiO$_2$, and an APTES monolayer on Si/SiO$_2$. These surfaces had advancing water contact angles that were initially between ca. 30 and 50°. After stamping, the water contact angles of these surfaces increased by ca. 6−9°, their ellipsometric thicknesses also increased by ca. 6−9 Å, and the percentage of the m/z 73 and 147 PDMS peaks in their ToF-SIMS spectra was high: 32−40%. These changes in properties are generally less than those for the clean silicon, titanium, and gold surfaces and are consistent with our hypothesis that PDMS transfer decreases as surface hydrophobicity increases.

The next group of surfaces (spin-coated polystyrene and our dodecyl and hexadecyl monolayers) had initial water contact angles in the range of ca. 90−100°. These water contact angles are similar to that of the PDMS stamp. Consequently, PDMS transfer to these surfaces would not be expected to change the water contact angles of these surfaces significantly, as is observed. We noted, however, that ca. 5 Å of material does transfer to these surfaces after stamping. The percentage of main PDMS peaks in the ToF-SIMS spectra is also rather high: 21−24%. Overall, the changes in physical properties for this group of surfaces is smaller than for the group with lower water contact angles that preceded it.

The final group (the perfluoro and Teflon materials) contained two very hydrophobic surfaces. Their advancing water contact angles were initially 108 and 118°, respectively. After stamping, the physical properties of these surfaces scarcely change. Their water contact angles and ellipsometric thicknesses remain essentially constant, and little or no PDMS is observed in their ToF-SIMS spectra. PDMS oligomers do not appear to transfer effectively to these hydrophobic surfaces, presumably because such a transfer would raise their surface free energies.

XPS was particularly useful in indicating chemisorption of PDMS on surfaces that did not initially contain silicon. The clean gold surface was 100% Au (no measurable Si) by XPS before stamping but showed substantial contamination after stamping: 28.2 ± 2.6% C, 20.5 ± 0.6% O, 15.2 ± 2.4% Si, and 36.1 ± 0.3% Au. The clean Ti/TiO$_2$ surface contained 20.9 ± 1.3% C, 59.0 ± 0.1% O, 20.1 ± 1.3% Ti, and no measurable Si before stamping but 31.3 ± 1.6% C, 46.0 ± 5.8% O, 4.6 ± 0.9% Si, and 14.8 ± 1.2% Ti after stamping. The spin-coated polystyrene surface was 100% C by XPS before stamping but 95.6 ± 1.2% C, 2.8 ± 0.7% O, and 1.6 ± 0.5% Si after stamping. Finally, the Teflon surface, which was 29.3 ± 0.2% C, 11.0 ± 0.0% O, 0% Si, and 59.7 ± 0.3% F before stamping, showed essentially no change after stamping: 30.5 ± 0.2% C, 10.8 ± 0.0% O, 0% Si, and 58.7 ± 0.1% F.

Using eq 2, which is the equation of state for interfacial tension, solid−vapor surface tensions (γ_{sv}) were calculated for the surfaces in Table 1 from their water contact angles, from which the change in solid−vapor surface tension ($\Delta\gamma_{sv}$) after stamping was estimated. Table 1 clearly shows that the change in surface tension is greatest for the surfaces that initially were most hydrophilic, where stamping lowers their surface free energies. The degree to which the surface free energy is lowered decreases with increasing surface hydrophobicity until little change in this property is observed for the most hydrophobic surfaces. These results for $\Delta\gamma_{sv}$ are consistent with the other results in Table 1 for $\Delta\theta_a(H_2O)$, Δt, and the percentage of the ToF-SIMS spectra due to PDMS peaks. As an important graphical illustration of these trends, all of these properties, along with the percentage of the PDMS peaks in the ToF-SIMS spectra, are plotted in Figures 3 as a function of the cosine of the initial water contact angle of the surfaces.
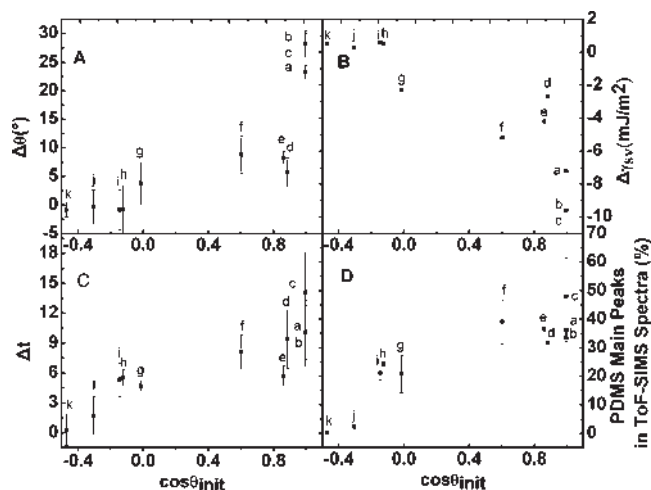
Figure 3. Changes in water contact angle (A), surface tension (B), and thickness (C) and percentage of PDMS main peaks in ToF-SIMS spectra (D) after stamping with PDMS for different surfaces. Clean Si/SiO$_2$ (a), clean Ti/TiO$_2$ (b), clean gold (c), dirty Si/SiO$_2$ (d), SiO$_2$/PEG monolayer (e), SiO$_2$/APTES monolayer (f), SiO$_2$/polystyrene (g), Si/dodecyl monolayer (h), Si/hexadecyl monolayer (i), SiO$_2$/perfluoro monolayer (j), and Teflon (k).
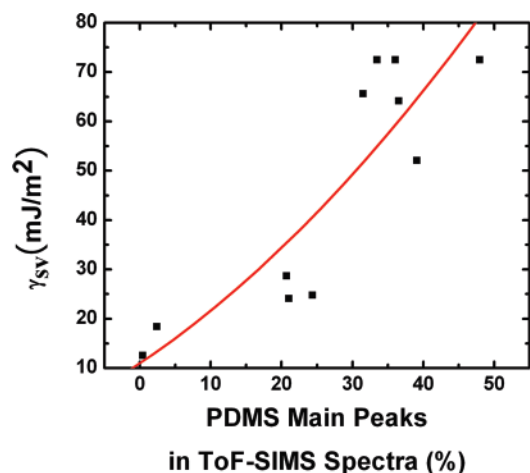

Figure 4. Relationship between the surface tension at the solid−vapor interface and the percentage of PDMS main peaks in the ToF-SIMS spectra of various surfaces.

These results point to a relationship between the surface tension of a material, γ_{sv}, and the percentage of the main PDMS peaks (%PDMS) in its ToF-SIMS spectra. Figure 4 shows a plot of γ_{sv} versus %PDMS. An approximate fit of this data to an empirical model is shown in Figure 4 and is given by $\gamma_{sv} = 0.0105(\%\text{PDMS})^2 + 0.961(\%\text{PDMS}) + 11.0$ with $R^2 = 0.77$. Admittedly, this relationship would be of little worth for a large planar surface because of the ease with which water contact angles can be measured, and a different relationship would most likely need to be determined if a different primary ion source was employed. However, this relationship would allow one to estimate the surface free energies of microscopic features on patterned surfaces.

PDMS Transfer to Patterned Surfaces and Probing Surface Energies by Imaging ToF-SIMS. The fact that surface free energy influences PDMS transfer caused us to question whether this method could be used as a tool for probing surfaces in SIMS imaging. Accordingly, we analyzed six patterned

surfaces. The first set consisted of hydrophobic monolayers on silicon that had been patterned with (presumably) hydrophilic spots. A perfluoro hydrophobic monolayer of Cl$_3$Si(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$ on Si/SiO$_2$ and a monolayer of 1-hexadecene on hydrogen-terminated silicon were patterned with a brief pulse of intense laser light through a microlens array to give a square pattern of ca. 40 μm spots spaced by 100 μm.[30] Monolayers of 1-dodecene and 1-hexadecene on hydrogen-terminated silicon were also patterned with vacuum UV light through a stencil mask to again prepare a series of spots that should be more hydrophilic than their hydrophobic backgrounds. The UV patterning method removes hydrocarbon adsorbates and creates silanol groups in spots, as previously demonstrated by wetting and XPS studies of planar, monolayer-coated substrates.[32] Such surface silanols might condense with silanol groups on PDMS oligomers, covalently attaching them to the spots. Less is known about the spots produced during microlens array patterning of surfaces because one is limited in the characterization tools available to probe these spots and it is not entirely clear how one would pattern larger areas in a manner representative of the technique.[30]

Figure 5 shows that, in general, little contrast is present in the SIMS images of the m/z 73 and 147 ions prior to stamping. The little contrast that is observed in a few of the cases may be a result of the data binning to ±0.3 amu around each integer mass value that was necessary for image creation and would possibly incorporate more than one signal within these ranges. There may also be a small amount of PDMS contamination in some cases, which is common in many materials. This open question regarding PDMS contamination is answered below after a multivariate curve resolution analysis of the images taken before stamping; only the PEG monolayer on Si/SiO$_2$ appeared to have any real PDMS contamination.

After stamping, Figure 5 shows that the hydrophilic/hydrophobic pattern that was created by microlens array or UV patterning becomes apparent in the m/z 73 and 147 ion images. The contrast in the patterned perfluoro monolayer is especially stark and is consistent with very low or nonexistent levels of PDMS transfer to these very hydrophobic background regions. A clear preference for PDMS transfer to the spots over the backgrounds is also present in the patterned hexadecyl and dodecyl surfaces, and this selective transfer is again consistent with rather hydrophobic backgrounds next to more hydrophilic spots. In particular, the two hexadecyl monolayers provide an effective graphical illustration of our results. These surfaces had water contact angles of 106 and 98 °C prior to UV and microlens array patterning, respectively. As would therefore be expected, the more hydrophobic surface has the lower background signal (improved contrast) in the ToF-SIMS image after stamping (Figure 5). As noted, UV patterning may also create silanol groups in the spots,[32] leading to covalent modification at the spots and improved image contrast.

An interesting and very significant change in PDMS transfer occurs with patterned APTES and PEG monolayers. In these cases, PDMS has a greater tendency to transfer to the backgrounds over the spots in the microlens array patterned surfaces. We regard these results as remarkable in that they suggest that microlens array patterning of these important surfaces creates spots that are more hydrophobic than their background areas. Water contact angles of the spots created by the microlens array can thus be estimated to be above those of their respective APTES and PEG surfaces. Similarly, the water contact angles of the spots on the dodecyl, hexadecyl, and perfluoro surfaces should be lower than those of their
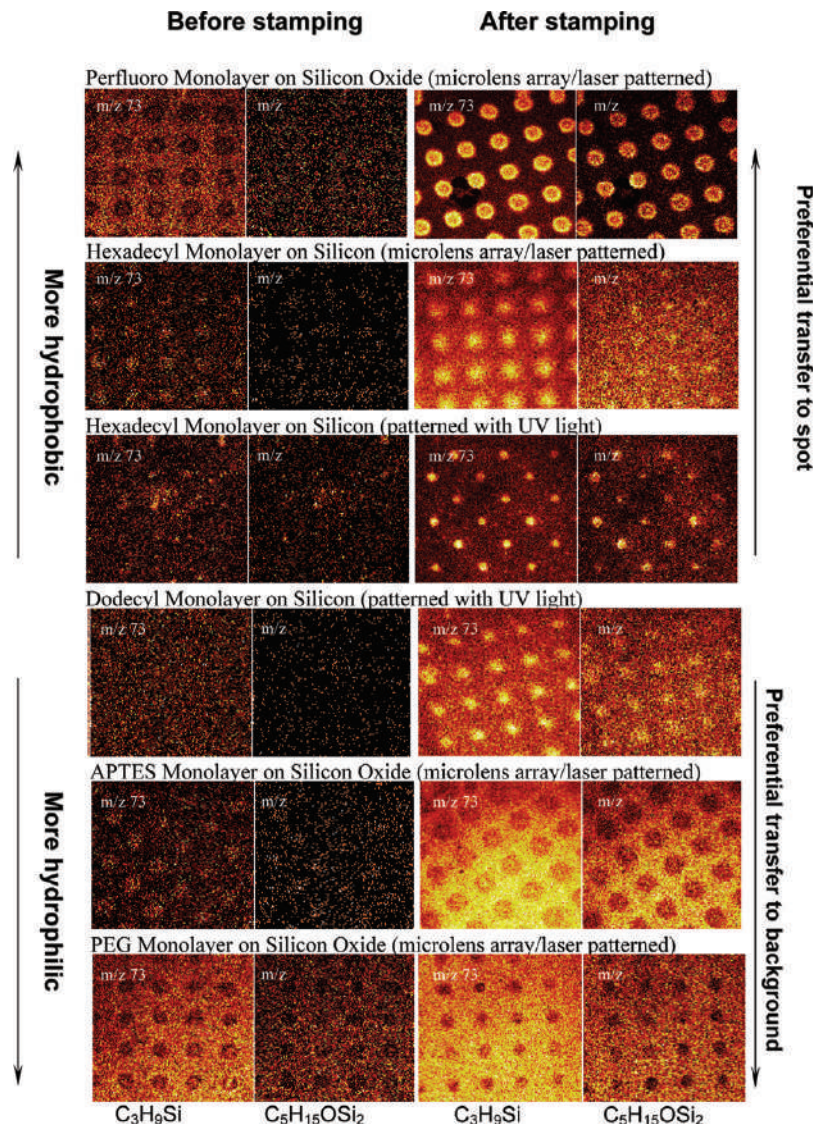
Before stamping   **After stamping**

Perfluoro Monolayer on Silicon Oxide (microlens array/laser patterned)

Hexadecyl Monolayer on Silicon (microlens array/laser patterned)

Hexadecyl Monolayer on Silicon (patterned with UV light)

Dodecyl Monolayer on Silicon (patterned with UV light)

APTES Monolayer on Silicon Oxide (microlens array/laser patterned)

PEG Monolayer on Silicon Oxide (microlens array/laser patterned)

C_3H_9Si $C_5H_{15}OSi_2$ C_3H_9Si $C_5H_{15}OSi_2$

Figure 5. Positive ion ToF-SIMS images (500×500 μm^2) for various surfaces before and after stamping with PDMS. SIMS images were collected at m/z 73 and 147 by binning to ± 0.3 amu around each integer mass value.

backgrounds. These results on the PEG monolayer surface are consistent with our recently published study[30] that showed selective protein adsorption to the spots of a microlens-array-patterned PEG monolayer surface. The obvious implication of these later results is that microlens array patterning of PEG monolayers destroys, and/or even chars, PEG surfaces, producing moderately hydrophobic spots to which proteins selectively adsorb. Protein adsorption to hydrophobic surfaces is a well-known phenomenon.

Multivariate curve resolution (MCR) is an important chemometrics tool for analyzing complicated data sets, including ToF-SIMS spectra. A priori, the MCR analysis of the ToF-SIMS data sets shown in Figure 5 was expected to reveal two main components, one associated with the spots and another with the background area. For all of the data sets except one, MCR analysis revealed three to five chemical components, where the number of components was determined using eigenvalue analysis.[44] Whatever the total number of components used to describe each image, they are grouped as background (component A),

spot (component B), and general components (component C). Figure 6 shows these grouped components with their percent variances for the perfluoro, dodecyl (UV), and APTES surfaces. (The three other surfaces are shown in the Supportng Information). Compared to the univariate analysis shown in Figure 5, MCR analysis often provides higher image contrast because the image is represented by a full spectral signature and not just one species.

Figure 6a shows all components of the MCR analysis of the images taken before stamping, where the perfluoro, dodecyl (UV), and APTES monolayers on Si/SiO_2 do not have any noticeable PDMS contamination (no peaks at m/z 73 and 147; see components A and B) (i.e., these results are consistent with the original ToF-SIMS spectra, which did not show PDMS contamination). For the APTES and perfluoro surfaces, contrast between spots and background is seen before stamping. It is significant that for the dodecyl surface (UV) essentially no contrast is observed before stamping, which is also consistent with the ion images shown in Figure 5.

Figure 6b shows the MCR components of the perfluoro, dodecyl (UV), and APTES surfaces after stamping. The perfluoro surface is primarily described by two MCR components,

(44) Keenan, M. R. In *Techniques and Applications of Hyperspectral Image Analysis*; Grahn, H., Geladi, P., Eds.; John Wiley & Sons: Chichester, U.K., 2007.
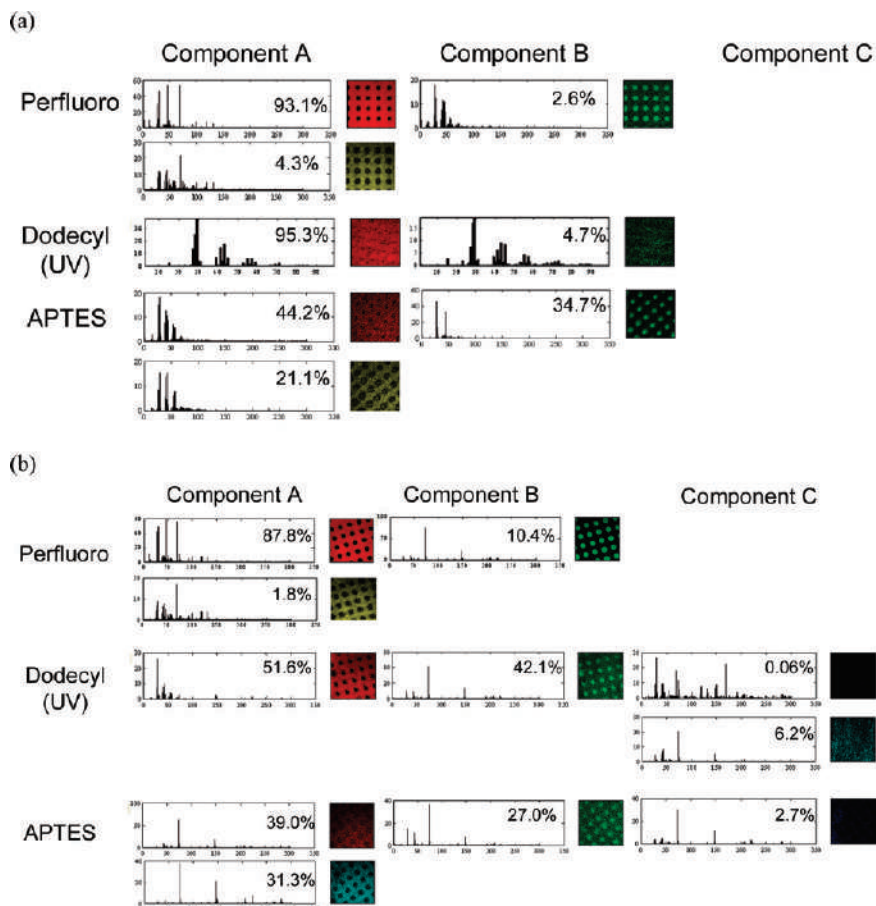
Figure 6. MCR spectra (loadings plots), associated images (scores plots), and the corresponding percentage of variance in each data set of three grouped MCR components corresponding to the background area, spots, and overall area before stamping (a) and after stamping (b).

which, like the raw data in Figure 6a, show high contrast. The three largest peaks in the background component (A) are at m/z 31, 47, and 69, which correspond to CF^+, SiF^+, and CF_3^+, respectively. These peaks would be expected from a perfluorinated material. There is also a minor background component. Neither of the background components contains PDMS ions. In contrast, the spot component (B) is almost exclusively due to PDMS, which confirms PDMS transfer to the spot and not the background, and suggests that the spot created by microlens array patterning is more hydrophilic than its background. The dodecyl (UV) surface is described by four MCR components. There is a background component (A) that shows essentially no PDMS, a significant spot component (B) that contains a strong PDMS signals, and one significant overall component that reveals PDMS. In contrast to the MCR results from the perfluoro surface, these results show focused PDMS transfer to hydrophilic spots along with some PDMS transfer over the entire surface, which is consistent with the greater PDMS transfer to these substrates suggested in Table 1 (vide infra). It is noteworthy that PDMS transfer revealed chemical contrast in this patterned surface that was not obvious in the ToF-SIMS or even MCR images prior to stamping. The APTES surface is again described by background, spot, and overall components. However, all of these components contain PDMS signals. These loading spectra appear to vary only in the degree to which they contain PDMS. This result and that in Figure 5 are consistent with a significant amount of PDMS transfer to the APTES surface (Table 1) and with the formation of a more hydrophobic surface that also imbibes some PDMS oligomers.

This analysis clearly increases our understanding of the data in Figure 5.

Discussion

Perhaps the first mention of the possibility of contamination during μCP was in 1997 by Larsen and co-workers.[45] They studied microcontact-printed monolayers of dodecanethiol on Au(111) using scanning tunneling microscopy (STM) and wetting. They reported that there was no evidence of surface contamination from the PDMS stamp. There are two ways to view their conclusions. The first is that the techniques that they used to analyze their surfaces, STM and wetting, lack, to some degree, chemical specificity, so they may not have been able to see any contamination that may have been present, although it should be noted that the authors were able to obtain reasonably high resolution STM images of the monolayers, which suggests that the level of any surface contamination was low. The other possibility, which we favor, is that little or no PDMS contamination was present on the surfaces because, as our results suggest, little or no PDMS contamination occurs on very hydrophobic surfaces. The results of Larsen and co-workers need to be weighed against the subsequent report of Böhm,[5] who reported significant PDMS contamination in microncontant-printed hexadecanethiol-on-gold monolayers, even though the monolayers were quite hydrophobic. To explain why others had not previously observed PDMS contamination during μCP, Böhm and co-workers noted the rather high

(45) Larsen, N. B.; Biebuyck, H.; Delamarche, E.; Michel, B. *J. Am. Chem. Soc.* **1997**, *119*, 3017–3026.

pressures that they applied during printing. (A comparison of results between laboratories is somewhat challenging because different groups typically use different conditions to prepare PDMS stamps and printing conditions may also vary from laboratory to laboratory.)

Sharpe and co-workers[22] recently reported that "the extent of the PDMS-containation is dependent on the nature of the ink used." They arrived at this conclusion because much more PDMS contamination was observed when μCP on gold was performed with a hydrophilic ink (16-mecaptohexadecanoic acid, MHDA), than with a hydrophobic ink (*n*-octadecanethiol, ODT). They reported a control experiment consisting of μCP using MHDA and ODT on monolayers that were preformed from MHDA and ODT, respectively. PDMS contamination was strong in the case of the MHDA monolayer, but none was observed on the ODT film. This latter result is consistent with the earlier report of Graham and co-workers.[7]

We wish to qualify the emphasis of Sharpe and co-workers that it is the hydrophilicity/hydrophobicity of the ink that primarily determines PDMS transfer during μCP. That is, our findings are consistent with their interpretations to the extent that hydrophilic inks produce hydrophilic surfaces, which adsorb PDMS, and that hydrophobic surfaces produce hydrophobic surfaces, which resist PDMS adsorption. That is, the ink itself in the stamp may have less to do with PDMS transfer to substrates than the surface free energies of the films produced from the inks. In the case of an ink that takes a significant amount of time to assemble at a surface, it may be the underlying substrate that largely determines the degree of PDMS contamination, as least for short contact times between the stamps and the substrates.

We are also not entirely comfortable with Sharpe and co-worker's proposal that it is primarily hydrophilic PDMS oligomers that are the contaminating species in μCP. Whereas some of the material that is transferred from the stamp during μCP probably is hydrophilic, we believe that our results and those of previous researchers are more consistent with the idea that hydrophobic oligomers of PDMS are the primary contaminants that are observed in μCP. We give the following reasons. First, it has been repeatedly shown by other researchers (vide supra) and now by us that PDMS contamination of surfaces during μCP generally makes them more hydrophobic, which is consistent with the transfer of a hydrophobic species. In addition, hydrophilic surfaces having high free energies are well known to be spontaneously contaminated with less hydrophilic materials to reduce their surface free energies. A classic example of this phenomenon is the spontaneous contamination of clean, native oxide-terminated silicon wafers with adventitious hydrocarbons upon exposure to the laboratory environment. The resulting surfaces, which were originally wet by water, are fairly hydrophobic. In addition, we note that NMR has shown that most of what is removed by Soxhlet extraction

from PDMS stamps is silicones,[20] although in partial support of the Sharpe hypothesis a relatively small fraction of this material was thought to be hydrophilic. Finally, FTIR and ToF-SIMS have repeatedly shown the characteristic signals of poly(dimethyl-siloxane) after μCP (vide supra), including those signals that confirm the presence of the (hydrophobic) methyl groups of this polymer.

The decomposition of transferred PDMS into submicrometer droplets[46] should not be an issue for the relatively large (tens of micrometers) features studied in this work, especially because the practical resolution of our instrument for organic materials is on the order of a micrometer.

Conclusions

The transfer of polydimethylsiloxane (PDMS) to a series of patterned and unpatterned surfaces with different surface free energies has been observed by time-of-flight secondary ion mass spectrometry (ToF-SIMS), wetting, and spectroscopic ellipsometry. PDMS transfers to hydrophilic surfaces or even moderately hydrophobic surfaces. However, hydrophobic surfaces (e.g., Teflon, perfluoro, or alkyl monolayers with high advancing water contact angles) resist the adsorption of PDMS. On patterned surfaces, PDMS transfers to hydrophilic spots patterned onto hydrophobic monolayers but not onto the hydrophobic background, or it transfers preferentially onto more hydrophilic backgrounds. Surface free-energy calculations from wetting results help explain PDMS transfer. MCR analysis of ToF-SIMS images on patterned surfaces reveals that PDMS transfers to different areas according to the properties of background monolayers and patterned features. Our results strongly suggest that PDMS stamps can effectively probe these materials. In addition, this study provides a correlation between surface free energies based on the relationship between the fraction of peaks due to PDMS in ToF-SIMS spectra and the surface free energy. These results have obvious implications for traditional microcontact printing with PDMS stamps.

Supporting Information Available: Other experimental results, including ToF-SIMS spectra of stamped surfaces, additional MCR analyses of ToF-SIMS images, and a short segment of Matlab code used in our chemometrics analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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