



Supporting Information

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Supporting Information to

Universal Ink for Microcontact Printing

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Materials and Methods

Materials. The stamp material, Sylgard-184 Poly(dimethylsiloxane) (PDMS), was obtained from Dow Corning. It was mixed in a 1:10 curing agent/prepolymer ratio, cured overnight at 65°C, and post-cured for at least 4 weeks at room temperature. Stamp replication was performed in contact with a silicon master bearing either no pattern (flat stamps) or various electronic test patterns (relief patterned stamps). Silicon wafers were modified with an about 500 nm thick thermal silicon oxide layer, a titanium adhesion layer (5 nm, evaporated) on top, and finally with an evaporated gold layer with a thickness of 10 nm (“gold substrates”). Prior to use, gold substrates with a size of $1 \times 2 \text{ cm}^2$ were rinsed with, subsequently, ultrapure water (resistivity $>18 \text{ M}\Omega \times \text{cm}$), ethanol, and heptane. They were thereafter exposed to a TEPLA 300E microwave argon plasma (0.25 mbar Ar, 300 W, 5 min). Glass plates were cleaned by rinsing successively with soap solution, water, and isopropanol. After drying, a 50 nm thick aluminum layer was deposited by evaporation immediately prior to use (“aluminum substrates”). It was found to be critical to keep the time between aluminum evaporation and SAM deposition short. Delay times were therefore generally not longer than about two hour.^[1] Octadecanethiol (ODT, 98% purity, Sigma-Aldrich), octadecylphosphonic acid (ODPA, 95% purity, PolyCarbon), hydrogen peroxide (31% solution, Merck), ethanol, isopropanol, and n-heptane (all p.a. grade, Merck) were used as received. Ink solutions were freshly prepared before each set of experiments by dissolving ODT and/or ODPA in ethanol. Dissolution was supported by immersion in an ultrasound bath for about 10 minutes.

Microcontact Printing and Etching. PDMS stamps (about $1 \times 2 \text{ cm}^2$) were equilibrated for a minimum of four hours in the corresponding ink solutions. After removal from the ink solution, all stamps were rinsed briefly with ethanol and dried in a stream of nitrogen for about 30 seconds immediately prior to use. Stamping was performed manually by using tweezers for stamp handling and by taking advantage of the natural stamp-substrate adhesion. Contact times were 15 s for gold and three minutes for aluminum substrates. Printed aluminum samples were post-treated on a hot plate (65°C) for 10 min.^[1,2] All stamped samples were etched at room temperature in open polyethylene containers using freshly prepared etching baths. The gold etchant was composed of $\text{K}_2\text{S}_2\text{O}_3$ (0.1 M), $\text{K}_3\text{Fe}(\text{CN})_6$ (0.01 M), and $\text{K}_4\text{Fe}(\text{CN})_6$ (0.001 M) in aqueous KOH (1.0 M) solution containing n-octanol at half saturation.^[3,4] The aluminum etchant contained 0.1 wt% hydrogen peroxide in an alkaline solution (KOH, pH 12.0), which was half saturated with n-octanol.^[5]

Stamp analysis (sulfur) by combustion and ion chromatography. PDMS stamps were inked as described above. They were dried for one minute in a stream of nitrogen and then overnight in an ambient atmosphere. Pieces of PDMS stamps (about 80 – 110 mg) were subjected to Wickbold combustion using a H_2/O_2 flame. Gaseous products were collected in an aqueous 0.75% H_2O_2 solution to obtain sulfate products. Their concentration was determined by ion chromatography using a Dionex DX 500 system, with an AS-14A column and a carbonate/bicarbonate eluent. The obtained concentrations were translated to ODT concentrations after correction for background contributions, which were determined from triple blank analyses of PDMS stamps that were treated with neat ethanol following the above inking protocol, in each set of experiments. Molar concentrations were calculated using a PDMS density of 1.05 kg dm^{-3} .

Stamp analysis (phosphorus) by combustion and inductively coupled plasma – atomic emission spectrometry (ICP-AES). Wickbold combustion followed by ion chromatography did not yield highly reproducible results in the case of phosphorus analysis, and the total phosphorus recovery was less than 90%. An alternative analysis method was therefore used. PDMS stamps were prepared as described above. Pieces of inked PDMS stamps (about 80 - 110 mg) were placed in a crucible, which contained a droplet of isopropanol. The crucible and an absorbing liquid (an aqueous sodium carbonate solution) were placed in a “Parr-bomb”, which was then filled with dioxygen

(30 bar). Stamp and isopropanol were in contact with a platinum wire, which allowed for an electrical initiation of the combustion reaction. Following the reaction, an hour was allowed for the absorption of gaseous products into the absorbing liquid. The obtained solution and the remaining silicon body were transferred to a platinum crucible, to which hydrofluoric, perchloric, and nitric acid were added. The platinum crucible was irradiated with a 300 W lamp to remove silicon and carbon components until a solid residue was obtained, which was redissolved in diluted nitric acid. Total phosphorus concentrations of this solution were determined by ICP-AES analysis using a Jobin Yvon 238 ICP atomic emission spectrometer (Power: 1200 Watt, Plasma Gas flow: 12 l/min, $\lambda_{em}(P) = 178.225$ nm). The obtained concentrations were translated to ODPa concentrations after correction for background contributions, which were determined from triple blank analyses of PDMS stamps that were treated with neat ethanol following the above inking protocol, in each set of experiments. Molar concentrations were calculated using a PDMS density of 1.05 kg dm^{-3} .

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed using a Quantum 2000 instrument from Ulvac – PHI. All XPS data were acquired at a nominal photoelectron takeoff angle of 45° , where the takeoff angle is defined as the angle between the surface normal and the axis of the analyzer lens, using AlK_{α} -radiation providing an information depth of about 6 nm. Areas of about $1200 \times 500 \mu\text{m}^2$ were scanned with a spot diameter of $100 \mu\text{m}$. All neutralizing beams (slow electrons, low energy ions) were switched-off during the analyses in order to prevent radiation damage. The raw atomic concentrations and the binding state of chemical species were determined on the basis of accurate narrow-scan measurements. CasaXPS^[6] was used for the analysis of the XPS-spectra (curve fitting and quantification of peak areas). The real concentrations and values for the layer thickness and coverage of the organic layers were obtained by means of model calculations.^[7] The samples were assumed to have the following structure: metallic substrate (Al or Au), sulfur (as Au-thiolate) and phosphorus at the metal surface, organic top layer. For the Inelastic Mean Free Path reported values were used.^[8] Analyses were usually performed in duplicate; average values are reported provided that the spreading of individual results was less than 10% of the reported average value.

Atomic Force Microscopy. AFM analysis was performed on a Veeco MultiMode scanning probe microscope with a NanoScope IV controller. Etched substrates were analyzed in non-contact (tapping) mode using an Ultrasharp μ Mash NSC16 type A cantilever.

References

- [1] L. B. Goetting, T. Deng, G. M. Whitesides, *Langmuir* **1999**, *15*, 1182-1191.
- [2] M. Geissler, H. Wolf, R. Stutz, E. Delamarche, U.-W. Grummt, B. Michel, A. Bietsch, *Langmuir* **2003**, *19*, 6301-6311.
- [3] M. Geissler, H. Schmid, A. Bietsch, B. Michel, E. Delamarche, *Langmuir* **2002**, *18*, 2374-2377.
- [4] Y. Xia, X.-M. Zhao, E. Kim, G. M. Whitesides, *Chem. Mater.* **1995**, *7*, 2332-2337.
- [5] P. M. S. John, H. G. Craighead, *Appl. Phys. Lett.* **1996**, *68*, 1022-1024.
- [6] CasaXPS version 2.2.52, <http://www.casaxps.com>.
- [7] C. van der Marel, M. Yildirim, H. R. Stapert, *J. Vac. Sci. Technol. A* **2005**, *23*, 1456-1470.
- [8] P. J. Cumpson, *Surf. Interface Anal.* **2001**, *31*, 23-34.