

Tailoring SU-8 Surfaces: Covalent Attachment of Polymers by Means of Nitrene Insertion

Venkataraman V. Nagaiyanallur,^{†,||} Deepak Kumar,^{†,⊥} Antonella Rossi,^{†,§} Stefan Zürcher,^{†,‡} and Nicholas D. Spencer^{*,†}

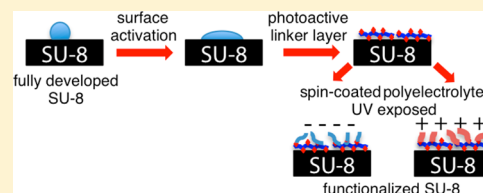
[†]Laboratory for Surface Science and Technology, Department of Materials, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

[‡]SuSoS AG, Lagerstrasse 14, CH-8600 Dübendorf, Switzerland

[§]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Campus di Monserrato, S.S. 554 bivio per Sestu, I-09100 Cagliari, Italy

S Supporting Information

ABSTRACT: The photoresist material SU-8 has found a variety of applications in microfabricated systems, such as microelectromechanical (MEMS) and lab-on-a-chip devices. Although the bulk properties of SU-8 are appropriate for many such applications, tailoring its surface-chemical properties has, until now, proven to be challenging but is essential in order to carry out any subsequent self-assembly steps. We have demonstrated that the SU-8 surface can be functionalized by the covalent grafting of a wide variety of polymers by means of nitrene insertion. This is readily achieved with poly(allylamine)-*graft*-perfluorophenyl azide (PAAm-g-PFPA) or poly(ethyleneimine)-*graft*-PFPA (PEI-g-PFPA), which can form covalent bonds to both the SU-8 surface and a functionalizing polymer. As examples, poly(diallyl-dimethylammonium chloride) (PDDA) and poly(styrenesulfonate) (PSS) have been covalently linked to a SU-8 substrate, yielding positively and negatively charged surfaces, respectively. The grafted polymers were characterized by means of X-ray photoelectron spectroscopy, and their charge characteristics were confirmed via charged-particle adsorption.



1. INTRODUCTION

SU-8 is a commonly used, epoxy-based negative photoresist. The bulk properties of SU-8, such as its rigidity, chemical stability, low cellular toxicity, and transparency to visible light, have led to its frequent use in a variety of applications in microelectromechanical systems (MEMS),^{1,2} lab-on-a-chip,^{3,4} microfluidics,⁵ biomimetics,⁶ bio/chemical sensing,⁷ and DNA and protein immobilization.⁸ Although its bulk properties are highly desirable, the natural hydrophobicity of SU-8 can present serious problems, resulting in undesired adsorption of biomolecules or poor wetting by aqueous solutions in microchannels.⁹ The modification of SU-8 surface by means of physical adsorption and wet-chemical or plasma treatments has been reported. To'a Salazar et al.¹⁰ and Wang et al.¹¹ have shown the physical adsorption of biomolecules (fibronectin and collagen) onto SU-8 surfaces to enable cell attachment. Nordström et al.¹² suggested a widely used^{4,10,12–14} wet-chemical modification of SU-8 based on etching with cerium(IV) ammonium nitrate (CAN) and ethanolamine, which can yield a hydrophilic surface. The main limitation of this method is that it leads to the accumulation of cerium species on the surface.¹³ Simply dipping SU-8 surfaces into sulfuric acid can induce surface charge,⁴ but this approach is limited to electrostatic adsorption applications. Wu et al.¹⁵ have proposed that it is possible to permanently modify SU-8, rendering its surface hydrophilic, by forming a copolymer with

glycidol and SU-8. Although hydrophilic SU-8 surfaces can also be readily achieved through oxygen-plasma^{4,10,12,13,16} treatment, it is not stable in the long term, leads to a roughening,¹⁶ and is therefore only of limited utility for applications.

Surface functionalization with polymers, on the other hand, is an extremely flexible approach to modifying surface chemistry because the variety of polymers with different properties (e.g., hydrophilic, biocompatible, biofunctional, charged, conducting) is virtually limitless. A host of different methods has been proposed for grafting polymers onto SU-8 surfaces. Kim et al.¹⁷ proposed a polymer-grafting approach based on swelling–deswelling and demonstrated the grafting of PEG (poly(ethylene glycol)) onto 2D and 3D SU-8 patterns. This process is limited by a long incubation time of 12 h. UV-mediated grafting of poly(acrylic acid) and other water-soluble monomers to SU-8 has been proposed by Wang et al.¹¹ This method also has limitations: (i) it is not suitable for fully-developed SU-8 because it relies on the presence of residual SU-8 photoacid generator and (ii) the active layer is too thick (several micrometers) for sensor applications. Several authors have succeeded in growing polymer chains from an SU-8 surface. This is effective, while highly specific and labor-

Received: April 5, 2014

Revised: June 16, 2014

Published: August 6, 2014

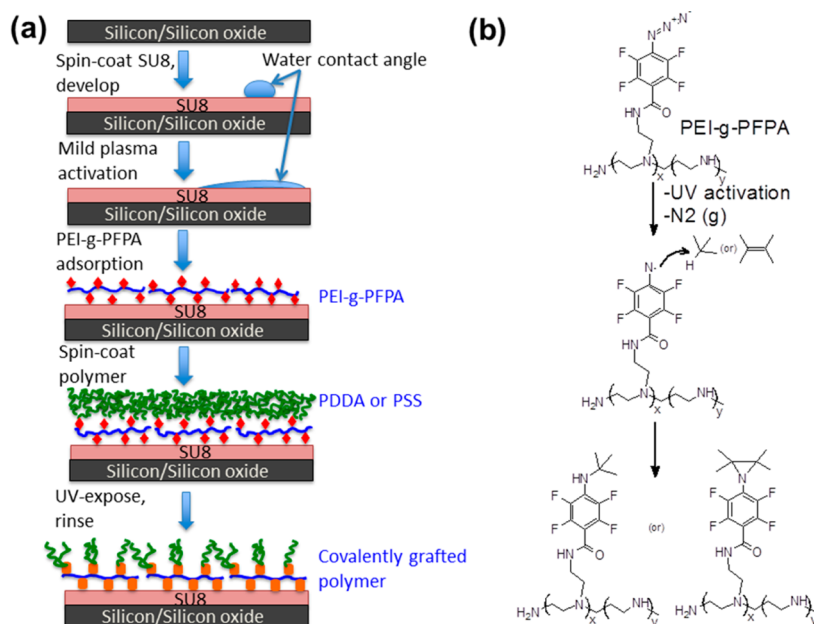


Figure 1. (a) Process flow of covalent grafting of polymers onto SU-8 surfaces and (b) the possible mechanism of formation of covalent bonding between SU-8 and the polymer.

intensive: Gao et al.¹⁸ grafted a *p*-HEMA (poly-2-hydroxyethyl methacrylate) film onto SU-8 by photopolymerization with 1-hydroxycyclohexyl phenyl ketone as a surface-bound initiator. Wang et al.¹⁰ reported grafting of polymers to an SU-8 surface via atom-transfer radical polymerization (ATRP), using a cerium(IV) catalyst. Saravanan et al.¹⁹ reactively incorporated hydroxylated perfluoropolyether molecules into the SU-8 during curing, thereby rendering the surface lubricious.

Here, we propose a simple, highly versatile approach to grafting a wide range of polymers onto SU-8 surfaces. A photoactivated linker, poly(ethyleneimine)-*graft*-perfluorophenyl azide (PEI-g-PFPA) or poly(allylamine)-*graft*-perfluorophenyl azide (PAAm-g-PFPA) is used to covalently bind the polymers of interest to a SU-8 surface. As examples, the charged polymers poly(diallyldimethylammonium chloride) (PDDA) and poly(styrenesulfonate) (PSS) have been used to generate positively and negatively charged surfaces, respectively. The charge characteristics are confirmed by electrostatic adsorption of positively and negatively charged particles.

2. EXPERIMENTAL SECTION

SU-8 was obtained from Gersteltec, Switzerland. The photoactivated linkers poly(allylamine)-*graft*-perfluorophenyl azide (PAAm-g-PFPA) and poly(ethyleneimine)-*graft*-perfluorophenyl azide (PEI-g-PFPA) were synthesized by reacting appropriate quantities of *N*-hydroxysuccinimide-PFPA (NHS-PFPA) obtained from SuSoS AG, Switzerland, with either PAAm or PEI as previously described for PAAm-g-PFPA.^{20–23}

The reactions were carried out overnight in a dark glass vial protected from ambient light. The synthesis of PEI-g-PFPA was carried out in pure ethanol as solvent, and that of PAAm-g-PFPA, in a 3:2 mixture of ethanol and HEPES (10 mmol) buffer. The grafting ratio (defined as the number of amino groups per PFPA group used in the synthesis) was maintained at 4 for all of the experiments described here. Both graft copolymers worked well for the surface modification: in the case of PEI-g-PFPA, the grafting ratio is limited to a maximum of 4 by the available primary amino groups in the backbone (approximately 25% of the total amino groups), whereas in the case of PAAm, even lower grafting ratios can be accessed. Freshly synthesized polymer stock solutions were diluted to a concentration

of 0.1 mg/cm³ in ethanol (for PEI-g-PFPA) or in 3:2 ethanol/HEPES (for PAAm-g-PFPA) for surface modification of SU-8. Poly(diallyldimethylammonium chloride), MW ~ 8500 (PDDA), and poly(sodium 4-styrenesulfonate), MW ~ 70 000 (PSS), were obtained from Polysciences Inc. (Warrington, PA, USA) and Sigma-Aldrich (Switzerland), respectively. They were used as received. Bare silica microparticles (~0.9 μm) and amidine latex particles (~0.2 μm) were obtained from Micro-Particles GmbH (Germany) and Invitrogen (Molecular Probes, USA), respectively.

The SU-8 surface was prepared by spin-coating, baking, UV exposure, postexposure baking, and developing of SU-8 on a silicon wafer using the standard protocol from the manufacturer.²⁴ The developed SU-8 surface was activated with a brief (30 s) air-plasma treatment (Plasma Cleaner/Sterilizer, PDC-32G instrument, Harrick, Ossining, NY, USA) and then immersed into a 0.1 mg/cm³ solution of PEI-g-PFPA in ethanol for 1 h. After removal from solution, the samples were thoroughly rinsed with ethanol, followed by drying in a stream of nitrogen, after which they were immediately spin-coated (1 min at 500 rpm, followed by 1 min at 3000 rpm) with aqueous solutions (10 mg/cm³) of PDDA or PSS. Subsequently, they were exposed to 254 nm UV radiation for 5 min. The conditions for spin-coating and the UV irradiation time have been chosen according to previously published results.²⁰ A nonspecific photochemical reaction initiated at the PFPA moieties covalently links the SU-8 surface with the polymeric chains of the top layer that are directly in contact with the linker layer. Finally, the sample was thoroughly rinsed with water to remove the unbound polymer, leaving the SU-8 surface with a covalently bound layer of PDDA or PSS. The process flow of surface functionalization of SU-8 is shown schematically in Figure 1.

2.1. X-ray Photoelectron Spectroscopy (XPS). The SU-8 sample surfaces were investigated by means of small-area X-ray photoelectron spectroscopy (XPS) using a Quantera SXM (ULVAC – PHI, Chanhassen, MN, USA) at each stage of surface modification: before and after surface functionalization with graft copolymer and subsequently with PDDA and PSS. The X-ray source is monochromatic Al Kα, and the emission angle θ is 45°. Samples were mounted on a standard plate, and a beam diameter of 200 μm was used; survey spectra were acquired with a power of 46.5 W, a pass energy of 280 eV, and a step size of 1 eV; detailed spectra were acquired using a pass energy of 69 eV and a step size of 0.125 eV (the full-width at half-maximum of the peak height of the Ag 3d_{5/2} spectrum is 0.72 eV under these conditions). Assuming lateral

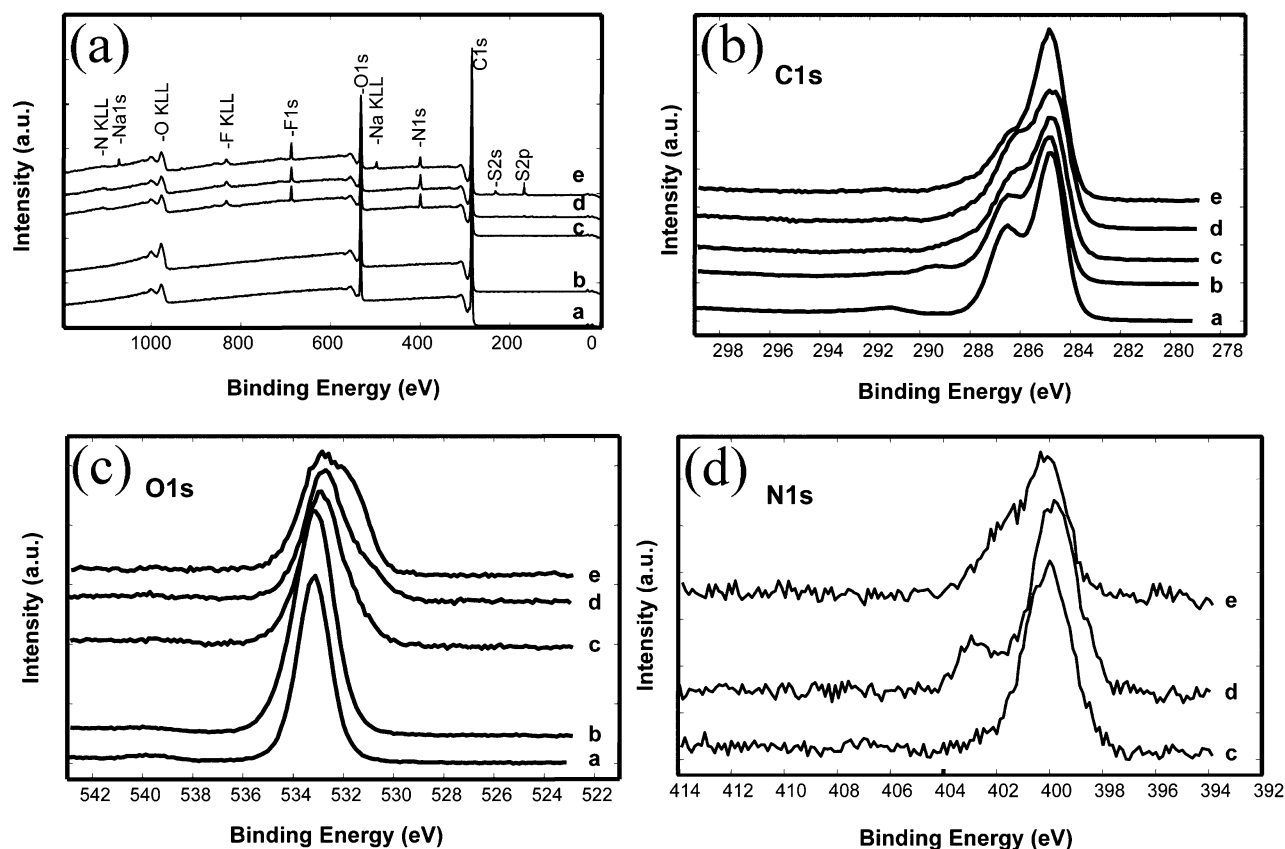


Figure 2. XPS spectra of the SU-8 surface after each step of the functionalization process depicted in Figure 1: (a) survey, (b) C 1s, (c) O 1s, and (d) N 1s spectra. Individual traces: a, SU-8; b, plasma-treated SU-8; c, PEI-g-PFPA on SU-8; d, PEI-g-PFPA on SU-8 with immobilized PDDA; and e, PEI-g-PFPA on SU-8 with immobilized PSS.

homogeneity of the surfaces, C 1s, O 1s, and N 1s were acquired at first on different points of the samples in order to avoid artifacts due to sample degradation under the X-ray beam. The base pressure was always maintained below 5×10^{-7} Pa. To compensate for sample charging during the analyses, low-energy electrons and ions were used (1 V, 20 A), and C 1s was taken as an internal reference at 284.8 eV. The linearity of the binding-energy scale was checked according to ISO 15472:2001, and the accuracy was better than 0.05 eV. Detailed spectra were processed using CASAXPS software (v. 2.3.15, Casa Software Ltd, Wilmslow, Cheshire, UK). Detailed surface characterization is presented for PEI-g-PFPA modified SU-8. The results for PAAm-g-PFPA-modified SU-8 samples were qualitatively similar.

2.2. Adsorption of Particles. Adsorption of the charged microparticles was carried out by immersing the polymer-grafted surfaces into an aqueous suspension of silica or amidine latex particles, which were allowed to settle for 2 to 3 min. Aizenberg et al.²⁵ have suggested that charged colloidal particles deposit in two steps: attachment of colloids to the substrate and an additional ordering of the structure upon drying. Here, after removal from the suspension, the samples were briefly immersed in ethanol, and the surface was dried in a stream of dry nitrogen, which removed the loosely adsorbed particles, after which they were in a packed and stable configuration.

2.3. Atomic Force Microscopy (AFM). Topographical images of the surfaces were recorded using an AFM MFP-3D (Asylum Research, Santa Barbara, CA, USA). The measurements were performed in air using tapping mode. The cantilever used for imaging was obtained from Olympus Corporation, Japan, with a nominal stiffness of 23 N/m.

2.4. Contact-Angle Measurements. In order to determine the contact angle after surface activation, a contact-angle goniometer (DSA-10; Krüss GmbH, Hamburg, Germany) was used under ambient conditions (21 °C; relative humidity, 48–52%) with deionized water as a probing liquid. The tangent method was used for the

determination of contact angles. Data from at least three drops per wafer were averaged.

3. RESULTS AND DISCUSSION

3.1. Surface Characterization. XPS spectra were acquired after each functionalization step following the scheme shown in Figure 1. The survey spectra with the detailed C 1s, O 1s, and N 1s regions are shown in Figure 2. The main signals in the survey spectra belong to SU-8 constituents (C and O): the appearance of the nitrogen and fluorine signals confirms the presence of PEI-g-PFPA or PAAm-g-PFPA polymer. The appearance of additional signals from S 2p and Cl 2p after reaction with PSS and PDDA, respectively, confirms the presence of the polyelectrolyte layer on top. The high-resolution spectra showing the C 1s signal indicates it to be asymmetric and composed of three components at 284.8, 286.5, and 291 eV. After air-plasma treatment, a C 1s component at higher binding energy (289.5 eV) substantiates the presence of oxidized species, whereas the shakeup signal at 291 eV, characteristic of aromatics, almost disappears. These changes are consistent with the changes in the water contact angle measured after plasma treatment, indicating the formation of oxidized carbon species, possibly as carboxylates, on the SU-8 surface.

After functionalization with PEI-g-PFPA, the functional polymers (PSS or PDDA), and UV-irradiation, the C 1s signal broadens due to the presence of an additional C–F contribution to the carbon peak. The O 1s signal exhibits the most significant change after reaction with PSS. The component at 531.6 eV also contains the contribution of the

sulfonate group and therefore increases following the reaction of the PSS with the PEI-g-PFPA. The nitrogen signal N 1s, absent in SU-8 and plasma-treated SU-8, is first detected following SU-8 functionalization with PEI-g-PFPA or PAAm-g-PFPA. Its shape is influenced by subsequent reaction with both PDDA and PSS. The presence of a distinct N 1s signal at higher binding-energy values (ca. 402.7 eV) in the case of PDDA-functionalized SU-8 could be assigned to the quaternary nitrogens of PDDA. The broader signal observed after reaction with PSS may be due to residual unreacted PAAm-g-PFPA that had been shielded from UV exposure by the highly absorbing PSS.

3.2. Surface-Charge Characterization. PDDA and PSS are positively and negatively charged polymers, respectively. The charge characteristics of the polymer-grafted SU-8 surfaces were tested by adsorption of bare silica and amidine latex particles. Figure 3 shows representative topographical AFM

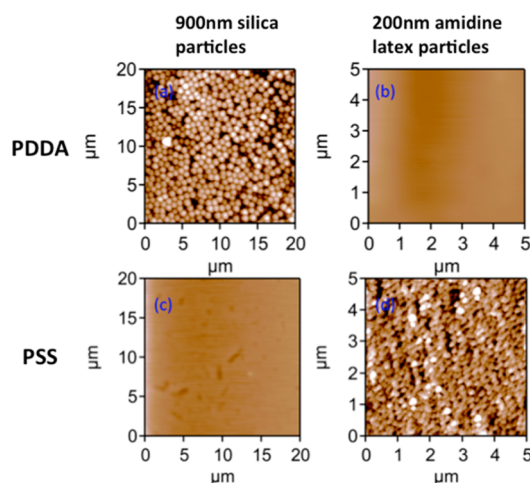


Figure 3. Topographical images obtained with AFM: (a) electrostatically adsorbed bare silica (negatively charged) particles on a PDDA (positively charged)-functionalized SU-8 surface. (b) No amidine latex particles (positively charged) adsorb on this surface. (c) No silica particles adsorb on a PSS (negatively charged)-functionalized SU-8 surface. (d) Amidine latex particles adsorb on a PSS-functionalized surface.

images following exposure of PDDA- or PSS-grafted SU-8 surfaces to either the bare silica (negatively charged) or amidine latex (positively charged) particles. The presence of bare silica particles on PDDA-grafted SU-8 surfaces (Figure 3a) and their complete absence on PSS-grafted surfaces (Figure 3c) is consistent with the expected charges. Similarly, amidine latex particles were found to adsorb on the PSS-functionalized SU-8 surface (Figure 3d), whereas they did not adsorb onto the PDDA-functionalized SU-8 surface (Figure 3b).

The developed SU-8 surface contains free epoxy groups, and its interaction with air/oxygen plasma has been previously reported.^{13,26,27} It is widely accepted that exposure of polymers to plasma can create specific binding sites or modify the surface chemistry by cross-linking, chain scission, or incorporation of functionalities.^{26,27} We expect that a hydrophilic surface is generated on SU-8 following plasma treatment due to the generation of C=O and COO[−] groups at the surface,^{26,28} and the low water contact angle is consistent with this assumption. However, this effect is temporary, as the plasma-modified SU-8 surface recovers its hydrophobic character within a few hours of

storage in air. When the plasma-treated surface is further subjected to chemical modification, as described herein, the resulting surface retains its hydrophilic properties over a much longer time due to the formation of stable covalent bonding between the applied polymer and the SU-8 surface (see the Supporting Information). The XPS results provide direct qualitative evidence that the SU-8 surface is successfully functionalized first with PAAm-g-PFPA or PEI-g-PFPA and subsequently either with PDDA or PSS, rendering the final surface positively or negatively charged, respectively. The reaction mechanism of polymer immobilization with PFPA has been extensively investigated in a previous publication.²⁹ Further confirmation of the presence of different chemical functional groups may be provided by infrared spectroscopy, which is more sensitive to specific functional groups. However, such measurements have proven to be difficult, as conventional surface-sensitive IR methodologies are not readily applicable to SU-8 surfaces.

4. CONCLUSIONS

This work presents the covalent functionalization of SU-8 surfaces with two very chemically different charged polymers, poly(diallyldimethylammonium chloride) (PDDA) (positive) and poly(styrenesulfonate) (PSS) (negative). The grafting of the polymers was achieved by means of the photoactivated linkers, poly(allylamine)-g-perfluorophenyl azide (PAAm-g-PFPA) or poly(ethyleneimine)-g-perfluorophenyl azide (PEI-g-PFPA). Unlike other reported methods for SU-8 functionalization, this approach is highly versatile and very straightforward, as the polymers to be attached do not need to be end-functionalized with surface-active or specifically reactive end groups. Therefore, due to the nonselectivity of nitrene insertion, this functionalization approach can be used to attach a wide variety of functional polymers²² onto SU-8 and other polymeric surfaces, presenting a wealth of possibilities for the incorporation of microfabricated SU-8 components into systems for many different applications, as well being as a general platform for polymer functionalization.

■ ASSOCIATED CONTENT

Supporting Information

Static water contact angles measured on plasma-activated SU-8 and plasma-activated PDDA grafted SU-8 measured after different periods of storage. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nspencer@ethz.ch. Tel.: +41 44 632 58 50.

Present Addresses

^{||}(V.V.N.) Mahindra Ecole Centrale, Bahadurpally, Jeedimetla, Hyderabad 500043, India.

[⊥](D.K.) Centre for Industrial Tribology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India.

Notes

The authors declare the following competing financial interest(s): The azide-containing polymers reported in this article are manufactured by SuSoS AG, of which Stefan Zürcher is Chief Technical Officer.

ACKNOWLEDGMENTS

The authors are grateful to the Swiss NanoTera project SELFSYS for providing funding and to Dr. Canet Acikgöz for her help in the preparation of the substrates.

REFERENCES

- (1) Zhang, J.; Tan, K. L.; Gong, H. Q. Characterization of the polymerization of SU-8 photoresist and its applications in micro-electro-mechanical systems (MEMS). *Polym. Test.* **2001**, *20*, 693–701.
- (2) Lorenz, H.; Despont, M.; Fahrni, N.; Brugger, J.; Vettiger, P.; Renaud, P. High-aspect-ratio, ultrathick, negative-tone near-UV photoresist and its applications for MEMS. *Sens. Actuators, A* **1998**, *64*, 33–39.
- (3) Antipina, M. N.; Kiryukhin, M. V.; Chong, K.; Low, H. Y.; Sukhorukov, G. B. Patterned microcontainers as novel functional elements for μ TAS and LOC. *Lab Chip* **2009**, *9*, 1472–1475.
- (4) Abgrall, P.; Conedera, V.; Camon, H.; Gue, A.-M.; Nguyen, N.-T. SU-8 as a structural material for labs-on-chips and microelectromechanical systems. *Electrophoresis* **2007**, *28*, 4539–4551.
- (5) Sikanen, T.; Tuomikoski, S.; Ketola, R. A.; Kostianen, R.; Franssila, S.; Kotiaho, T. Characterization of SU-8 for electrokinetic microfluidic applications. *Lab Chip* **2005**, *5*, 888–896.
- (6) Krijnen, G.; Floris, A.; Dijkstra, M.; Lammerink, T.; Wiegink, R. Biomimetic micromechanical adaptive flow-sensor arrays. *Proc. SPIE* **2007**, *6592*, 65920F.
- (7) Chang, C. Y.; Takahashi, Y.; Murata, T.; Shiku, H.; Chang, H. C.; Matsue, T. Entrapment and measurement of a biologically functionalized microbead with a microwell electrode. *Lab Chip* **2009**, *9*, 1185–1192.
- (8) Yang, B.; Dukkkipati, V. R.; Li, D.; Cardozo, B. L.; Pang, S. W. Stretching and selective immobilization of DNA in SU-8 micro- and nanochannels. *J. Vac. Sci. Technol., B* **2007**, *25*, 2352–2357.
- (9) Wang, Y.; Pai, J. H.; Lai, H. H.; Sims, C. E.; Bachman, M.; Li, G. P.; Allbritton, N. L. Surface graft polymerization of SU-8 for bio-MEMS applications. *J. Micromech. Microeng.* **2007**, *17*, 1371–1380.
- (10) To'a Salazar, G.; Wang, Y.; Young, G.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. L. Micropallet arrays for the separation of single, adherent cells. *Anal. Chem.* **2007**, *79*, 682–687.
- (11) Wang, Y.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. L. Simple photografting method to chemically modify and micropattern the surface of SU-8 photoresist. *Langmuir* **2006**, *22*, 2719–2725.
- (12) Nordström, M.; Marie, R.; Calleja, M.; Boisen, A. Rendering SU-8 hydrophilic to facilitate use in micro channel fabrication. *J. Micromech. Microeng.* **2004**, *14*, 1614–1617.
- (13) Walther, F.; Drobek, T.; Gigler, A. M.; Hennemeyer, M.; Kaiser, M.; Herberg, H.; Shimitsu, T.; Morfill, G. E.; Stark, R. W. Surface hydrophilization of SU-8 by plasma and wet chemical processes. *Surf. Interface Anal.* **2010**, *42*, 1735–1744.
- (14) Stangegaard, M.; Wang, Z.; Kutter, J. P.; Dufva, M.; Wolff, A. Whole genome expression profiling using DNA microarray for determining biocompatibility of polymeric surfaces. *Mol. Biosyst.* **2006**, *2*, 421–428.
- (15) Wu, C. L.; Chen, M.-H.; Tseng, F.-G. SU-8 hydrophilic modification by forming copolymer with hydrophilic epoxy molecule, 7th International Conference on Miniaturized Chemical and Biochemical Analysts Systems, Squaw Valley, CA, October 5–9, 2003.
- (16) Walther, F.; Davydovskaya, P.; Zürcher, S.; Kaiser, M.; Herberg, H.; Gigler, A. M.; Stark, R. W. Stability of the hydrophilic behavior of oxygen plasma activated SU-8. *J. Micromech. Microeng.* **2007**, *17*, 524–531.
- (17) Kim, H.-N.; Kang, J.-H.; Jin, W.-M.; Moon, J. H. Surface modification of 2D/3D SU-8 patterns with a swelling-deswelling method. *Soft Matter* **2011**, *7*, 2989–2993.
- (18) Gao, Z.; Henthorn, D. B.; Chang-Soo, K. Surface modification of SU-8 by photografting of functional polymers for lab-on-a-chip applications, 5th IEEE Conference on Sensors, Daegu, Korea, October 22–25, 2006; pp 121–123.
- (19) Saravanan, P.; Satyanarayana, N.; Sinha, S.K. Self-lubricating SU-8 nanocomposites for microelectromechanical systems applications. *Tribol. Lett.* **2013**, *49*, 169–178.
- (20) Sterner, O.; Serrano, A.; Mieszkun, S.; Zürcher, S.; Tosatti, S.; Callow, M. E.; Callow, J. A.; Spencer, N. D. Photochemically prepared, two-component polymer-concentration gradients. *Langmuir* **2013**, *29*, 13031–13041.
- (21) Serrano, A.; Sterner, O.; Mieszkun, S.; Zürcher, S.; Tosatti, S.; Callow, M. E.; Callow, J. A.; Spencer, N. D. Nonfouling response of hydrophilic uncharged polymers. *Adv. Funct. Mater.* **2013**, *23*, 5706–5718.
- (22) Soshee, A. K.; Zürcher, S.; Spencer, N. D.; Halperin, A.; Nizak, C. A. General in vitro method to analyze the interactions of synthetic polymers with human antibody repertoires. *Biomacromolecules* **2013**, *15*, 113–121.
- (23) Bielecki, R. M.; Crobu, M.; Spencer, N. D. Polymer-brush lubrication in oil: sliding beyond the stribek curve. *Tribol. Lett.* **2012**, *49*, 263–272.
- (24) Standard protocols for GM1075 or GM1040 from Gersteltec. <http://www.gersteltec.ch>.
- (25) Aizenberg, J.; Braun, P. V.; Wiltzius, P. Patterned colloidal deposition controlled by electrostatic and capillary forces. *Phys. Rev. Lett.* **2000**, *84*, 2997–3000.
- (26) France, R. M.; Short, R. D. Plasma treatment of polymers: the effects of energy transfer from an argon plasma on the surface chemistry of polystyrene, and polypropylene. A high-energy resolution X-ray photoelectron spectroscopy study. *Langmuir* **1998**, *14*, 4827–4835.
- (27) Akdogan, E.; Cokeliler, D.; Marcinauskas, L.; Valatkevicius, P.; Valincius, V.; Mutlu, M. A new method for immunosensor preparation: atmospheric plasma torch. *Surf. Coat. Technol.* **2006**, *201*, 2540–2546.
- (28) Olah, A.; Hillborg, H.; Vancso, G. J. Hydrophobic recovery of UV/ozone treated poly(dimethylsiloxane): adhesion studies by contact mechanics and mechanism of surface modification. *Appl. Surf. Sci.* **2005**, *239*, 410–423.
- (29) Zorn, G.; Liu, L.-H.; Arnadóttir, L.; Wang, H.; Gamble, L. J.; Castner, D. G.; Yan, M. X-ray photoelectron spectroscopy investigation of the nitrogen species in photoactive perfluorophenylazide-modified surfaces. *J. Phys. Chem. C* **2014**, *118*, 376–383.