Note: A single-chamber tool for plasma activation and surface functionalization in microfabrication

Adam J. Bowman,^{a)} Joseph R. Scherrer,^{a)} and Ronald S. Reiserer^{b)}

Vanderbilt Institute for Integrative Biosystems Research and Education and Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

(Received 13 January 2015; accepted 7 June 2015; published online 23 June 2015)

We present a simple apparatus for improved surface modification of polydimethylsiloxane (PDMS) microfluidic devices. A single treatment chamber for plasma activation and chemical/physical vapor deposition steps minimizes the time-dependent degradation of surface activation that is inherent in multi-chamber techniques. Contamination and deposition irregularities are also minimized by conducting plasma activation and treatment phases in the same vacuum environment. An inductively coupled plasma driver allows for interchangeable treatment chambers. Atomic force microscopy confirms that silane deposition on PDMS gives much better surface quality than standard deposition methods, which yield a higher local roughness and pronounced irregularities in the surface. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922827>]

Widespread application of microfluidics has benefited greatly from the use of soft-lithographic patterning of polydimethylsiloxane (PDMS).^{1,2} Central to this process is the bonding of PDMS devices with open-faced channels to either a glass slide or another PDMS film, block, or device. Plasma oxidation is a standard procedure for PDMS-PDMS and PDMS-glass bonding in which the bonding surfaces are made hydrophilic through exposure to a low-pressure air or oxygen plasma,³ typically generated within a small, inductively coupled plasma (ICP) cleaner (e.g., Harrick Plasma, Ithaca, NY) or even by a hand-held Tesla coil in air (e.g., Electro-technic, Chicago, IL). Energetic ions at the PDMS-plasma interface fragment methyl groups on the PDMS surface ($\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$) and replace them with silanol ($\text{Si}-\text{O}-\text{H}$) groups. These groups make the PDMS surface hydrophilic and enable strong covalent bonding to other surfaces terminated in hydroxyl groups.³ Plasma activation results in only temporary hydrophilicity,⁴ as the surface polymer chains reorient into the bulk, and unlinked oligomers migrate to the surface within a short time after exposure.^{5,6} The activation process is generally forgiving in terms of specific pressures and times and typically is optimized by each lab, often on a project-to-project basis that depends upon device design and even PDMS batch. This process is not to be confused with plasma cleaning or activation of surfaces in high-vacuum deposition systems.

While this plasma activation is suitable for immediate (in less than 1 min after extinguishing the plasma) bonding of PDMS to PDMS or glass, for example, in assembly of microfluidic devices, more permanent surface modification can be achieved by bonding silanes to the plasma-activated silanol groups on PDMS before they have a chance to migrate from the surface or otherwise react.³ Silanes can be terminated with functional groups that modify the PDMS surface

chemistry for a variety of applications. For example, specific silanes can facilitate double casting processes as a releasing agent,⁷ prevent molecule absorption,⁸ and improve surface wettability for solders.⁹ Treatment may be accomplished either by vapor¹⁰ or liquid phase³ deposition. We discuss vapor phase deposition methods for silanization. Common silane chemical vapor deposition (CVD) protocols are performed at pressures sufficiently low to support plasma ignition (0.1–2.0 Torr).^{7,10} Both the low cost and specialized nature of PDMS fabrication necessitate the use of off-the-shelf equipment in published protocols and discourage the use of costly commercial CVD equipment. Normally, the sample first undergoes plasma treatment in a plasma cleaner, after which it is transferred to a separate chamber, often a desiccator or vapor priming oven, and exposed to silane vapor evaporated from a dish or slide. This multi-chamber process (MCP) requires transfer between chambers and exposes the substrate to atmosphere between plasma activation and CVD steps. We believe that such exposure to atmosphere decreases surface reactivity and causes irregularities after treatment. Additionally, polymerization of silane by water vapor present in a MCP treatment chamber could cause surface irregularities on the substrate. Reduced surface roughness is desirable in both mold release and adhesion layers, as it improves surface conformality and pattern quality.¹¹

To address these problems, we have developed a compact treatment device (Figure 1) that can both plasma-activate a PDMS surface and perform chemical or physical vapor deposition (PVD) without exposing the sample mid-process to a humid laboratory environment, as is common in current treatment methods. Our single-chamber apparatus was constructed with a specific focus on silanization of PDMS for soft-lithography of microfluidic devices (Figures 1–3). It can also be used to silanize other surfaces that support covalently bound OH groups (e.g., glass, Si, SiC, graphene, and metal oxides).

The design allows the use of a single-chamber process (SCP) in which both plasma and vapor treatments take place in the same vacuum chamber, eliminating intermediate exposure

^{a)}A. J. Bowman and J. R. Scherrer contributed equally to this work.

^{b)}Author to whom correspondence should be addressed. Electronic mail: ron.reiserer@vanderbilt.edu.

FIG. 1. Plasma activation/CVD system schematic. The optional RF shielding is not shown.

to atmosphere and minimizing transition time between activation and vapor deposition steps. The design also provides a regulated low-pressure environment (50 mTorr–10 Torr). A modular reaction vessel and an ICP driver permit inexpensive chamber interchange, which is important for deposition processes sensitive to contamination. The ICP design also significantly reduces costs compared to commercial capacitively coupled CVD devices, as well as other ICP devices which require a vacuum port through the back of the chamber while remaining versatile and adaptable.

A 9 cm ID, 30 cm long Pyrex bell jar (components from Chemglass Life Sciences, Vineland, NJ) serves as the treatment chamber and sits inside the radio frequency (RF) coils that drive the ICP. The bell jar accommodates typical microfluidic devices, 7.5 cm and smaller silicon wafers, and ANSI/SLAS microplates. An acrylic tube machined to have a guide groove serves as the coil form. The aluminum base-plate seals to the bell jar flange with a Viton gasket and includes four 1/4 in. pipe thread (NPT) ports for the chemical injection septum, gas input valve, a chamber evacuation valve, and thermocouple gauge. The RF driver circuit is housed in a separate assembly to allow installation in a variety of configurations. As deposition on all chamber surfaces is expected during the chamber lifetime, the bell jar slides freely into and out of the coil mount for cleaning and replacement. The chamber is mounted to the outside wall of a ductless fume hood (AirClean Systems, AC3000, Raleigh, NC) through a 12.7 cm hole. This configuration allows chemical vapors to be extracted safely while providing hardware access from outside the hood. HCl vapors produced in chlorosilane deposition make corrosion inevitable, so all components in contact with the reactants and corrosive by-products are designed to be easily replaced.

FIG. 2. RF driver schematic. An Armstrong oscillator circuit is used with two 6FW5 pentode vacuum tubes in parallel.

FIG. 3. CVD apparatus mounted in fume hood (inset before mounting).

The ICP is excited in low pressure air between 0.1 and 2 Torr with a self-oscillating RF amplifier (Armstrong oscillator¹²), which runs at about 3.5 MHz and 20 W in the currently described configuration. A 550 V positive bias powers the circuit, and two 6FW5 pentode vacuum tubes are used in parallel for switching (V_1 and V_2). Oscillations are sustained in the tank circuit consisting of L_1 and C_4 . The pick-up or “tickler” coil L_2 couples inductively to L_1 and provides feedback to the tubes, which couple current into L_1 to sustain oscillation. Oscillator frequency is noncritical for activation but can be adjusted with C_4 . RF shielding may also be placed around the coil enclosure if desired to eliminate stray RF emission.

Vacuum is provided by a small rotary vane pump (VIOT, VPD3, Champaign, IL) and monitored with a thermocouple gauge (Kurt J. Lesker 615TC, Varian 531 tube). The user interface includes a digital timer to automate the treatment process and a delay relay to compensate for the tube filament heat-up time. Visual observations during operation indicate an approximately even distribution of plasma throughout the chamber. This evenness ideally contributes to consistency in treatment conditions.

The following PDMS silanization protocol was developed for apparatus characterization using trichloro (1H,1H,2H,2H perfluorooctyl) silane (PFOCTS) to create a more hydrophobic fluorocarbon coating.¹³ The PDMS samples used in all tests were made by pouring uncured PDMS (Dow, Sylgard 184 Silicone Elastomer) onto glass slides, degassing, and then curing for 10 min at 150°C, yielding 1 mm thick PDMS. The sample is first placed in the treatment chamber, which is then evacuated to approximately 500 mTorr. The plasma driver is activated and plasma is sustained for 40 s. After plasma treatment, the chamber is isolated from the pump and 100 μ l of silane is injected through the septum port, after which the sample is exposed to the silane vapor for 3–5 min. Finally, the chamber is vented and the sample retrieved. Contact angle was measured to be 124° with PFOCTS compared to 110° for untreated PDMS, demonstrating a hydrophobic surface coating. With no vapor treatment, the PDMS has a contact angle of <5° after plasma activation, reflecting hydrophilic silanol surface groups.

FIG. 4. AFM images of PDMS (a) unsilanized, (b) silanized with common MCP protocol, (c) silanized with our CVD apparatus (SCP), (d) large-scale irregularities in MCP silanized sample, (e) untreated PDMS (left) and thick SCP silane layer boundary (right) [note: scale is exaggerated due to plane fit—this is a ~ 40 nm film], and (f) sample over-oxidized in plasma, with resultant cracking.

Atomic force microscopy (AFM) was used to characterize treated PDMS surfaces. Uncoated PDMS was compared to PDMS treated with both conventional low-cost MCP methods and silanization in our SCP apparatus using the above protocol. To conduct common MCP methods with as few free treatment variables as possible, the MCP sample was treated with plasma in the present CVD device. However, instead of the vapor injection steps in the above protocol, the chamber was opened to expose the sample to atmosphere for 1 min after plasma treatment while silane droplets were added to a dish in the chamber. The chamber was then re-evacuated and sealed for 5 min, but the plasma was not activated. All AFM samples were treated in a prototypical device developed before the presented design was finalized. The prototype apparatus is functionally identical.

An atomic force microscope (Digital Instruments NanoScan III AFM, Santa Barbara, CA) was used for surface analysis. Samples were studied in tapping mode in atmosphere, using 10, 1, and $0.5\ \mu\text{m}$ scan sizes at 256 samples/line and a 1–2 Hz scan rate for roughness calculations. Surface roughness was calculated after applying a third-order plane fit to the raw data.

Figures 4(a)–4(d) show results from MCP and SCP treatments of PDMS. The MCP sample in Figure 4(b) exhibits a mean roughness (R_a) of 3.32 nm compared to 1.97 nm for the SCP sample (Figure 4(c)). At $10\ \mu\text{m}$ scan sizes, an R_a of 5.80 nm is observed for the MCP sample compared to 1.88 nm for the SCP sample. Deviations from the mean depth value increase at larger scan sizes with the MCP sample, indicating large-scale irregularities in addition to small-scale roughness. A $100\ \mu\text{m}$ scan of the MCP sample clearly demonstrates these large-scale variations, showing bubble-like structures and sharp vertical features (Figure 4(d)). The SCP samples show consistent surface roughness and deviations at

all scales. Improvement in quality for SCP over MCP demonstrates degradation of PDMS surface activation during MCP transfer and/or vapor phase polymerization due to water vapor present on re-evacuation.

Boundary layers were made by overlaying a separately fabricated, thin, spun PDMS membrane on a region of a sample during deposition in the SCP device and then removing the membrane before AFM measurement. Figure 4(e) shows the silane layer boundary. Data from several boundary trials indicate our standard protocol produces a silane layer ranging from 25 to 30 nm thick. Exposure time can be adjusted to tune layer thickness, and measured thicknesses between 5 and 40 nm have been achieved. Careful attention must be paid to each of the treatment parameters in order to achieve the desired surface, as indicated by Figure 4(f), which shows the effect of overexposing PDMS during plasma treatment. Overexposure forms a SiO_2 layer on the surface which displays rectilinear fracturing.¹⁴

We have designed an improved plasma-activated CVD apparatus for surface treatment in microfabrication that allows for improved coating quality over previous methods while maintaining affordability and customizability.

We thank John Fellenstein for advice on design, John Wikswo for comments on the manuscript, Allison Price for editorial assistance, and Lucas Hofmeister for assistance with contact angle measurements. This research was funded in part by DARPA 11-73-MPSys-FP-011, DTRA HDTRA1-09-1-00-13, and NIH NCATS 1UH2-TR000491-01 through the NIH Common Fund, the Vanderbilt Institute for Integrative Biosystems Research and Education, and the Systems Biology and Bioengineering Undergraduate Research Experience funded by Gideon Searle at Vanderbilt University.

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