Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2016

Supplementary information

Vapor-enhanced covalently bound ultra-thin films on oxidized surfaces for enhanced resolution imaging

Kexin Jiao, Chuanhong Zhou, Nathalie Becerra-Mora, Jared Fiske, Punit Kohli*
Department of Chemistry and Biochemistry
Southern Illinois University
Carbondale, IL 62901
*pkohli@chem.siu.edu

MATERIALS AND METHODS

Preparation of PDMS CVD film

Sylgard 184 silicone elastomer kit (Dow Corning) consists of two liquid components: the pre-polymer (A) and the curing agent (B). Only part A of Sylgard (PDMS pre-polymer without a curing agent) was used for PDMS SOLVED coating preparation. Poly(3,3,3-trifluoropropylmethylsiloxane) (F-PDMS) and (2-4% amino-ethyl-aminopropylmethylsiloxane)-dimethylsiloxane copolymer (N-PDMS) with branch structure purchased from Gelest were selected as siloxane molecules having fluoro- and amino-functional groups for SOLVED preparations. In general, 0.5g pure siloxane polymer without any initiator or crosslinking agent was spin-coated on a clean glass microscope slide substrate (75 mm x 25 mm x 1 mm) at 1000 rpm for 30 seconds. This treatment resulted in ~50 μm thick siloxane film on the substrate (called reservoir *R*). A surface such as glass, aluminum, or steel referred as surface (*S*) that needs to be coated was placed a distance of 1 mm above *R* (Scheme 1) and was placed in oven at ~150-250°C for 15-60 minutes. After cooling to room temperature, SOLVED coatings were sonicated prior to characterization.

Characterization of PDMS CVD film

Spectroscopic ellipsometry (SE) measurements. The SE measurements for PDMS coatings were carried out using a J. A. Woolley Co. M-2000 variable angle spectroscopic ellipsometer. The thickness measurements were performed on films deposited using SOLVED on Si wafers after coatings were sonication in toluene and ethanol for ~1 hour. The parameters for ellipsometry measurements were chosen from a similar work.[44] (A_n=1.4076; B_n= -0.5409; C_n= 0.1010; and

K=0). The refractive indices for the substrate (SiO_2) and coating were 1.47 and 1.41 respectively.

Contact angle (CA) measurement. CAs of water on PDMS CVD coated surfaces were measured using a CAM-Micro contact angle meter at room temperature. The functionalized surfaces were sonicated in toluene and ethanol for 1 hour prior to contact angle measurements. The water CA

Plasma etching study. The experiments for control of CA were performed using BSET EQ FA 2000™ Gas Plasma Solution Systems. After toluene sonication for 30 minutes, the functionalized substrates were faced down in plasma chamber in a mixture of 80% argon and 20% oxygen at an operating pressure of 200 mTorr as illustrated in Scheme S1. The radio frequency power was 50 Watts for all the experiments used in our plasma studies. The preparation of SOLVED samples for CA studies are described in result and discussion section. The control PDMS sample (1 mm thick) for water CA studies used for comparison with SOLVED films was prepared by curing a mixture of PDMS prepolymer (Sylgard 184) and curing agent at ratio of 10:1 at 100°C for 30 min.

FT-IR characterization. FT-IR data of all samples was collected on a Thermo-Nicolet Nexus 870 FT-IR spectrometer at 0.5 cm^{-1} resolution. The heated PDMS pre-polymer sample without crosslinking agent for FT-IR was prepared as a control by spin-coating 1 mg siloxane on gold coated silicon substrate at 5000 RPM for 30s followed by being heated at 250 ºC for 30 minutes. The PDMS and F-PDMS coated SOLVED samples for FT-IR were prepared using similar method described above on a gold coated silicon substrate using unpolymerized PDMS and F-PDMS respectively.

Thermal analysis. Thermal analysis of all samples was collected on a TGA Q50 from TA Instruments. The isothermal characterization was performed by heating the SOLVED samples to a desired isothermal temperature (T_i) at a ramp of 20°C/min then holding the temperature at T_i for 100 minutes. The total weight loss and the average weight loss rate at different T_i were collected. The weight loss rates at different temperatures were related to the evaporation rates of different components and therefore will suggest the effective component at out experimental conditions.

X-ray photoelectron spectrometry (XPS) characterization for SOLVED coatings. XPS analysis on SOLVED samples were performed on PDMS, F-PDMS, and N-PDMS SOLVED surfaces using Kratos Axis 165 Photoelectron Spectrometer after sequential sonication in toluene and ethanol for 1 hour each. Broad XPS surveys were performed for all the samples. Higher resolution scans for C 1s, F 1s, and N1s photoelectron regions were also performed for quantitative analysis. Ar ion sputter etching was performed on PDMS SOLVED samples for 30, 75 and 180 seconds respectively to gauge semi-quantitative SOLVED thickness on the surfaces. For all the XPS measurement, the SOLVED samples were coated on clean Si chips that possesses naturally formed 2-4 nm thick SiO_2 layer on the Si wafers. We did not use a special conductive surface for our experiments. However, we calibrated all the photoelectron peaks with respect to photoelectron peak at 285 eV of the C_{1s}-H in the $SiCH_3$ functionality.

Fabrication of Micro-lens (MLs) array on PDMS CVD film and imaging with MLs array. For MLs array fabrication, a PDMS SOLVED treated glass cover slide was selectively etched through a stainless steel mask with circular pores of 80 μm in diameter using reactive-ion etching (RF power = 50 Watts, Base pressure = 200 mTorr, gas = Argon 80% and oxygen 20%) for ~12 seconds. The etched glass slide was then flushed using saturated $ZnCl_2$ water solution resulting in MLs array. The glass cover slide with MLs array was attached on a Leica DM IRB optical microscope for further imaging and scanning. The images were captured in bright-field mode using a white light source and 10X objective (NA=0.2).

Cyclic voltammetry (CV). It is important to compare SOLVED coatings with well-studied coatings of similar properties to investigate how well SOLVED coatings perform against these coatings. For these studies, we have utilized covalently-bound octadecyltrimethoxysilane (OTMS) and tridecafluoro-1,1,2,2-tetrahydrooctyl-triethoxysilane (TTS) SAMs coated optically transparent ITO substrates as standard for PDMS and F-PDMS SOLVENT coatings respectively. ITO was used as a conductive electrode for probing $Fe(CN)_6^{2+}/Fe(CN)_6^{3+}$ redox reactions for SOLVED and SAM films using CHI700D electrochemical analyzer (CH Instruments). Siloxane-coated ITO electrodes were fabricated using SOLVED with PDMS and F-PDMS. SAMs coated ITO electrodes were fabricated by immersing clean ITO slide in 5% OTMS solution in ethanol with 1% glacial acetic acid (catalyst) for overnight followed by thorough ethanol rinsing. The ITO slide with OTMS SAM was heated at 100°C for 6 hours. TTS coated ITO electrode was fabricated using a similar method to that for OTMS SAMs but solvent used was 1:1 ethanol and chloroform mixture. The photostability comparison between SOLVED and SAMs coatings was performed by exposing SOLVED and SAMs coatings was performed to UV light source (365 nm) of ~0.5 mW/cm^2 intensity (model CL-1000, UVP Inc.). All CV characterization were performed in 5 mmol potassium ferric cyanide aqueous solution at scan rate of 0.1 Vs^{-1} from -0.4V to 1.0V scanning window.

Fluorescein and 9,10-Diphenylanthracene dual patterning on SOLVED surfaces. An F-PDMS SOLVED coating was argon-plasma etched for 7 s through a stainless stain mask with holes (150 μm) in it. The radio frequency power for Ar plasma was 50 W. Following plasma etching, the surface was flushed sequentially with 9,10-Diphenylanthracene (18 μM) in heptane and fluorescein (30 μM) dissolved in water. The fluorescence micrographs and spectra were taken using a Leica DM IRB microscope with a PerkinElmer Nuance hyperspectrometer CCD camera.

FDTD calculations. FDTA calculation for $ZnCl_2$ MLs was performed using Lumerical FDTD solution (version 15.0). A model comprising 2x2 MLs array with refractive index 1.6 on a 100 μm thick glass substrate was used for simulation studies. A total field scatter field (TFSF) light source with electric field amplitude of 30 units was set at 50 μm away from the back side of the glass substrate. The wavelength for the light source was 580 nm. The mesh size for the FDTD model was set to 500 nm.

Analysis of the contact angle of MLs.

The relationship between the curvature radius at vertex R and f is

$$f = \frac{R}{n(\lambda)-1} \qquad (2)$$

Therefore,

$$R = f(n(\lambda)-1) \qquad (3)$$

The estimated curvature radius is ~51 μm. Considering R is also given by

$$R = (K+1)\frac{h_L}{2} + \frac{r^2}{2h_L} \qquad (4)$$

where K is the aspherical constant. The value of K depends on the shape of lens profile. $K = 0$ for a spherical profile, $-1 < K < 0$ or $K > 0$ for elliptic profile, $K = -1$ for parabolic profile. From (4), we have

$$K = (R - \frac{r^2}{2h_L})\frac{2}{h_L} - 1 \qquad (5)$$

The calculated value for K is ~ 0.01, which indicate the $ZnCl_2$ MLs has spherical profile.

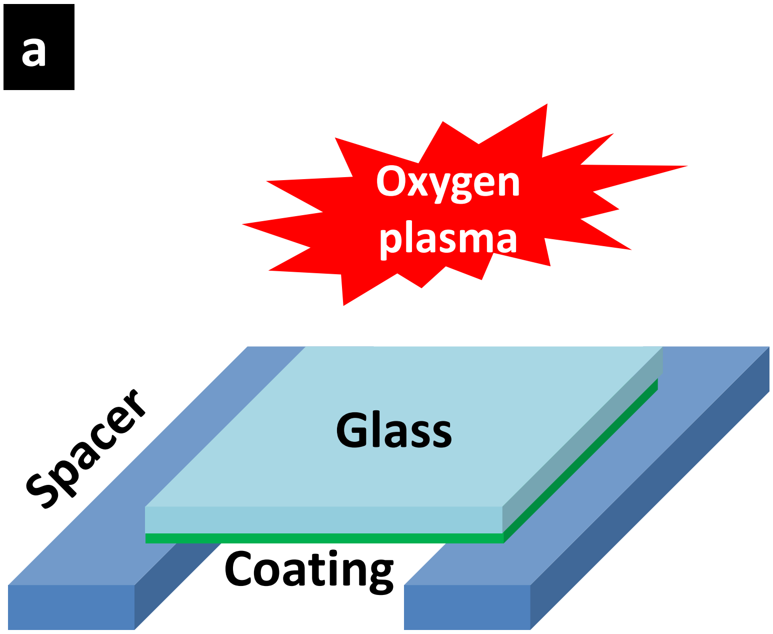
Furthermore, the CA of MLs can be estimated using

$$\sin\alpha = \frac{r}{R} \qquad (6)$$

Therefore,

$$\alpha = \sin^{-1}\left(\frac{r}{R}\right) \qquad (7)$$

The estimated α is ~48.5°, which is very close to our measurement.



Scheme 1S. The device setup during CA tuning using oxygen plasma. A glass cover slip with coating was placed face down (coated face down) on two 2 mm thick glass spacers. Oxygen plasma was applied from top.

Sample	**LTVD temperature** T **(°C)**	**Time to reach saturated CA** τ_{sat} **(min)**	**CA at** $\tau = 30$ **min**
A	100	N.A.	67.5
B	150	500	84.5
C	200	41	95.3
D	250	27	96.5
E	**300**	**23**	**97.8**

Table 1S. Temperature correlated saturation rate of different samples.

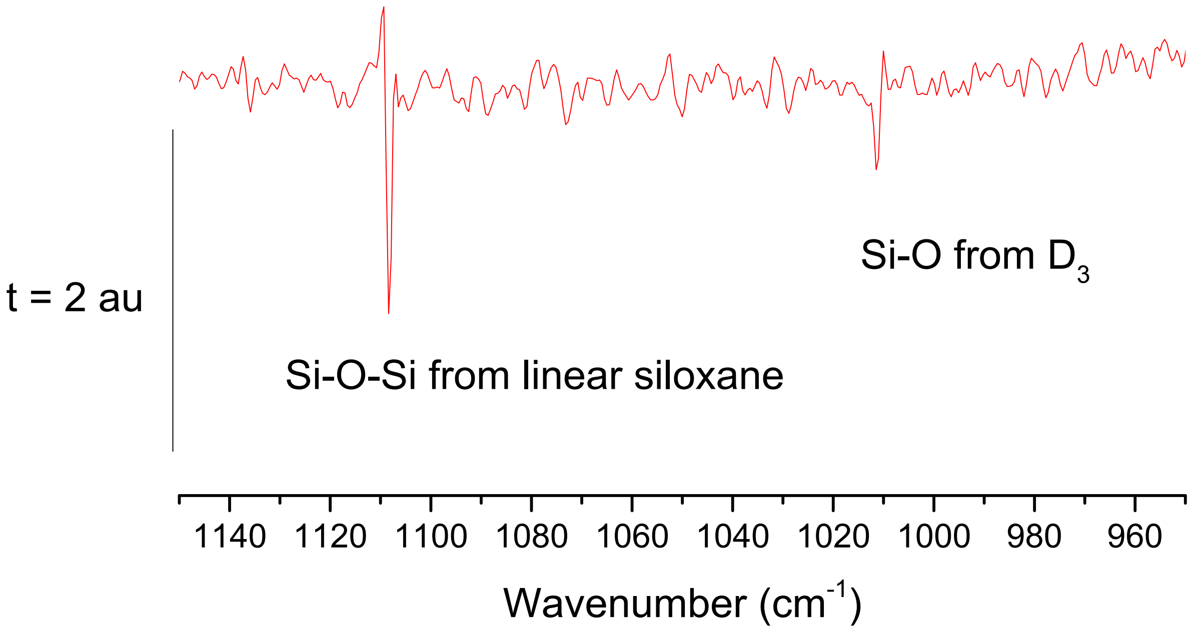


Fig. 1S. Si-O stretching in PDMS SOLVED coating on alumina. The peaks at 1011 cm^{-1} and 1107 cm^{-1} are due to Si-O from cyclic D_3/D_4 and linear siloxanes respectively. "*t*" represents transmittance in arbitrary units.

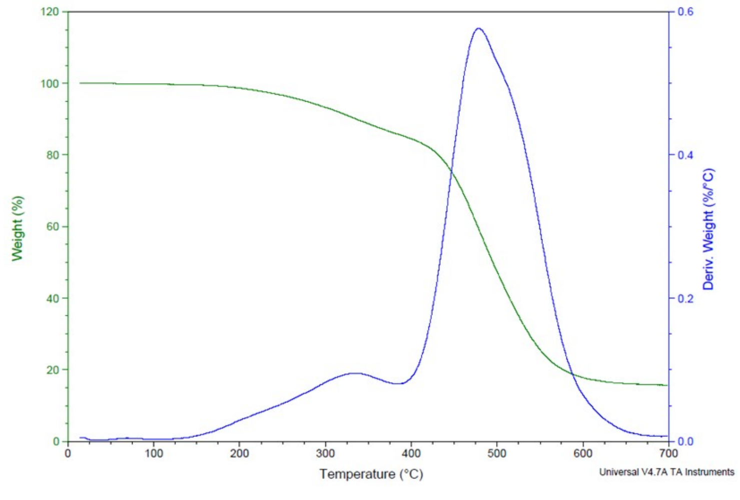


Figure 2S. TGA of PDMS prepolymer (temperature increase speed is 10˚C/min).

Less than 1% of weight loss was observed at a temperature lower than 280°C. This means that the most of the weight loss is due to loss of solvents present in the PDMS mixture. This points negligible PDMS degradation during PDMS SOLVED process which is performed at <250°C. A peak at ~ 330°C in derivated weight loss curve (blue color) represents the onset temperature of PDMS thermal degradation.

Functional groups	**Type of vibration**	**Characteristic Absorptions for bulk (cm^{-1})**	**Characteristic Absorptions for film (cm^{-1})**
C-H	C-H stretch	2850-3000	2961
Si-CH$_3$	Si-C stretch	1275-1245	1250
Si-CH$_2$CH$_2$CF$_3$	Si-C stretch	1218, 1130, 1070, 1025	1212 (strong)
CF$_3$	C-F stretch	1400-1000	1276 (very strong)
SiO	linear Si-O stretch	1000-1200	1090-1220 (strong)
SiO	cyclic D3 Si-O	1010-1020	1011 (weak)

Table 2S. IR frequency for functional groups in siloxane bulk materials and thin films.

	Wt%	**Boiling point (˚C) at 760 mmHg**
Dimethyl siloxane, dimethylvinyl-terminated	>60.0	~220
Dimethyl vinylated and trimethylated silica	30.0 – 50.0	2230[59]
Tetra(trimethylsiloxy) silane	1.0 – 5.0	222
Ethylbenzene	< 1.0	136
Xylene	< 1.0	138 - 144

Table 3S. Composition of commercial Sylgard 184 PDMS pre-polymer (part A).

Thermogravimetric analysis data. Commercially available PDMS prepolymer used for PDMS SOLVED formation is a mixture of multiple molecules and solvents.[68] The possible composition and their weight percentage and corresponding boiling points of many components of Sylgard 184 are shown Table 3S. TGA analysis was performed to assess the role of potential components in Sylgard 184 in the PDMS SOLVED films.

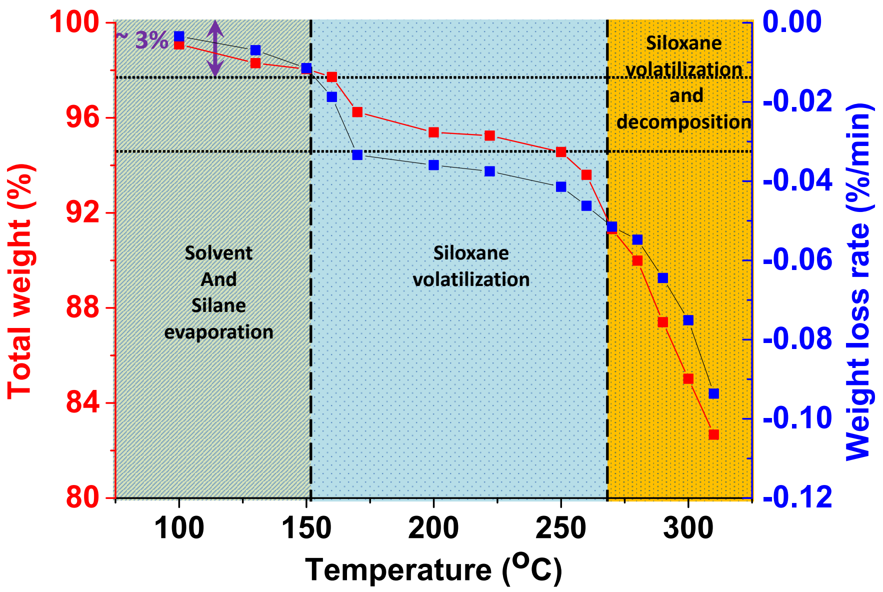


Figure 3S. Isothermal TGA and weight loss rate of PDMS prepolymer under different temperatures. The percentage weight loss and the weight loss rate were shown using red line and blue line respectively. Four domains were separated depending on heating temperature and weight loss.

Three distinct stages in ranges of 75-160°C, 160-260°C, and >260°C were observed in our thermogravimetric analysis (Fig. 3S). In 75°C-160°C region (green shade area, Fig. 3S), the weight loss was dominated by the evaporation of solvents (xylene and ethylbenzene) which make up <2.0% by weight in the PDMS prepolymer (Table 3S). A weight loss of 6% appeared in the 200°C-260°C range. According to manufacturer's data sheet,the possible constituents with BP in 160-260 °C possess ~60% weight in the prepolymer mixture are tetra(trimethylsiloxy)silane (TTMSS) (~222°C) and lower molecular weight siloxane components (~230°C). The observed weight loss value in this range ~6% was much smaller than reported on the manufacturer's data sheet. This is possibly due to chemical reactions occurring within the pan during heating that may yield other molecular products but without loss of the molecules.

We also performed the TGA weight loss isotherms from PDMS prepolymer in 100°C-300°C temperature range. Each heating process was performed under a given temperature and was maintained for 3 hours. The total weight loss and average weight loss rate of PDMS prepolymer under each temperature were recorded.

Discussion of effective component in PDMS pre-polymer during SOLVED. PDMS pre-polymer is a mixture of organic solvent; silane, siloxane, and silica (see Table 3S). All the components have opportunities to be deposited on glass surface during heating due to evaporation or the convection of atmosphere. We rule out solvents and silica as major contributor to the coating on the surfaces due to lack of reaction between surfaces and these species. We performed deposition using tetra(trimethylsiloxy)silane (the silane component in commercially available PDMS pre-polymer) under same experimental conditions as those used in the SOLVED with PDMS. The surfaces treated with tetra(trimethylsiloxy)silane showed water CA in 90° but with a large CA difference between spots for the same coated substrate. Therefore, tetra(trimethylsiloxy)silane showed some effectiveness for the surface modification but the water CAs were much smaller than that for PDMS/F-PDMS treated SOLVED films. Moreover, we also found that for ~0.5g PDMS pre-polymer reservoir, the siloxane source would be effective for ~ 10 trials at 250°C (~ 20 minutes for each trial length) for surfaces 1”x3”. After that, the siloxane source became less effective and resulted lower water CA (< 80°) on surfaces for over 2 hours SOLVED after sonication). Knowing that the weight percentage of TTMSS in PDMS pre-polymer (Sylgard 184) is less than 5%, the majority of TTMSS should be evaporated during the initial couple of trials. This result supports our conclusion that TTMSS is less likely that it is a major effective component for SOLVED films. Other evidence can be found from the fabrication of coatings with high CAs and low apparent diffusion coefficients using different pure siloxanes with different functional groups. To summarize, we would like to conclude that the major effective component in commercially available PDMS pre-polymer mixture contributing to SOLVED coating is the siloxane component.

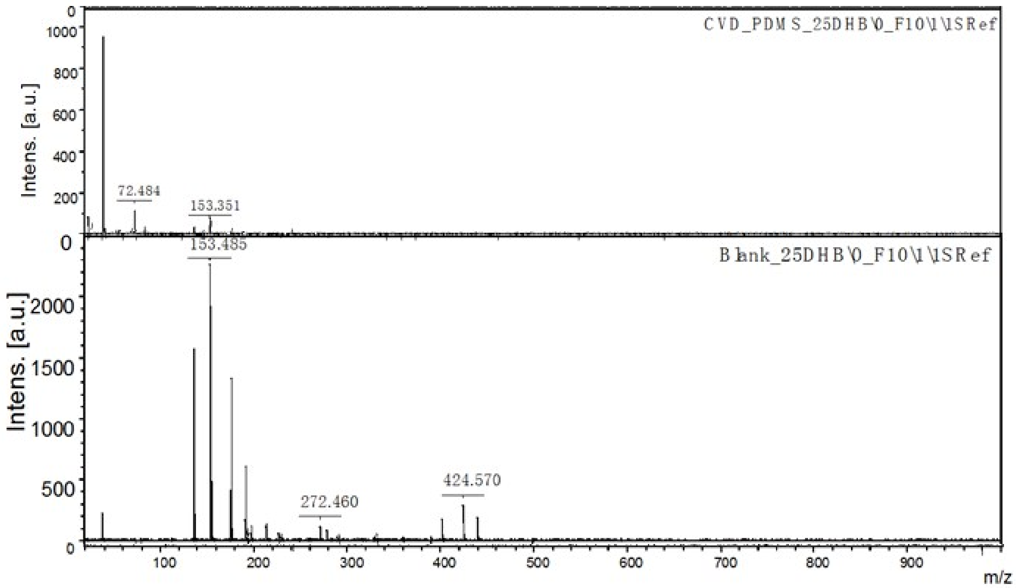


Figure 5S. MALDI-Mass spectrum for PDMS SOLVED coating (top) and Si (bottom).

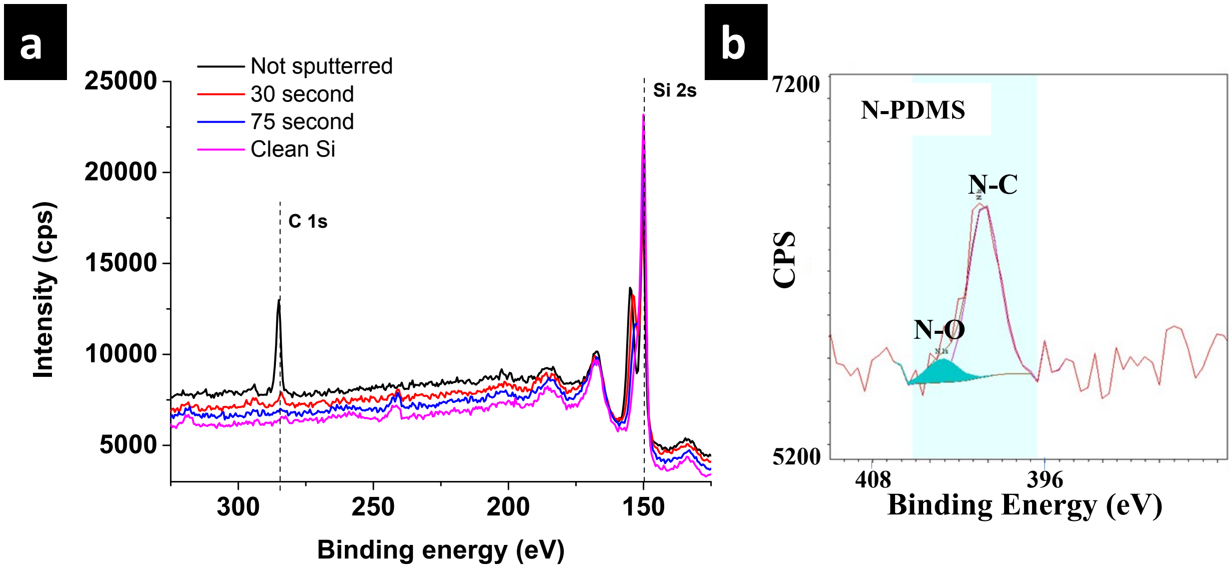


Figure 6S. (A) XPS results for PDMS SOLVED coatings on silicon surfaces with different argon sputter etching time under Argon. The C_{1s} peak at 285 eV decreases with sputtering time due to thinning of the polymer coating. Ar sputtering for 75 seconds lead to complete disappearance of C1s photoelectron signal suggested a complete removal of the coating on the surface. (B) A higher resolution N1s XPS region of N-PDMS SOLVED coating.

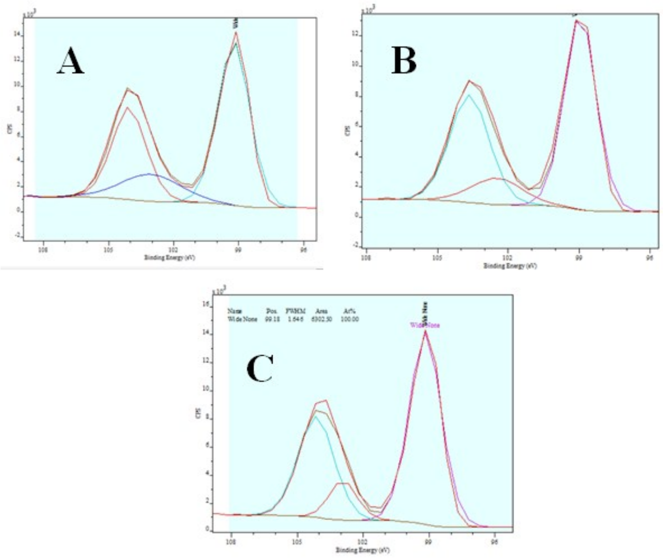


Figure 7S. Si2p XPS data for PDMS SOLVED (A), N-PDMS SOLVED (B), and F-PDMS SOLVED (C) films.

XPS analysis. The elemental composition-sputtered time data analysis on the PDMS SOLVED was performed to gain information on the thickness of the films (Fig. 6S). This analysis is semi-quantitative in nature and is used to collaborate with ellipsometric thickness data. A 30s Ar sputtering in XPS resulted in more than 6 times decrease in the [C1s]/[Si2p] photoelectron signal in XPS. The C1s signal originated from SOLVED films whereas Si2p signal resulted from both SOLVED and Si substrate. The [C1s]/[Si2p] signal ratio did not decrease significantly with further sputtering suggesting that the SOLVED films were almost completely etched within 30 s of the sputtering (Fig. 6S). A low signal-to-noise ratio for C1s peak and reliable C1s area integration for samples sputtered >30s did not allow us to perform quantitative analysis of the film thickness for these samples. With an approximate sputter etching rate of ~7.2 nm/min,[58] we semi-quantitatively estimate the PDMS SOLVED thickness is ~6 nm which is in agreement with our ellipsometry analysis.

SOLVED	Origin of the peak	BE (eV)	Atomic Conc. (%)
PDMS	**C1s$_{,\text{ total}}$**	**285**	**11.1**
	C1s-H, C1s-Si	285	10.0
	C1s-O	286.5	1.1
	Si2P$_{,\text{total}}$	**99-104**	**28.1**
	Si2p(0)	99.2	14.7
	Si2p(siloxane)	103.1	4.5
	Si2p(oxide)	104.1	8.9
F-PDMS	**C1s,$_{\text{ total}}$**	**285-293.2**	**9.3**
	C1s-H, C1s-Si	285	6.8
	C1s-O	286.2	1.5
	C1s-CF_3	293.2	1.0
	F1s	**688.5**	**5.5**
	Si2p	**99**	**34.0**
	Si2p(0)	99	18.7
	Si2p(siloxane)	102.9	2.9
	Si2p(oxide)	104.0	12.4
N-PDMS	**C1s$_{,\text{ total}}$**	**285-286.1**	**16.4**
	C1s-H, C1s-Si	285	12.3
	C1s-O, C1s-N	287.4	4.1
	N1s$_{,\text{ total}}$	**400.2-403.2**	**1.7**
	N1s-C	400.2	1.5
	N1s-O	403.2	0.2
	Si2p	**99**	**34.8**
	Si2p(0)	99	18.7
	Si2p(siloxane)	102.5	2.9
	Si2p(oxide)	103.6	12.4

Table 4S. XPS analysis of the covalently-bound SOLVED films of three different functional groups.

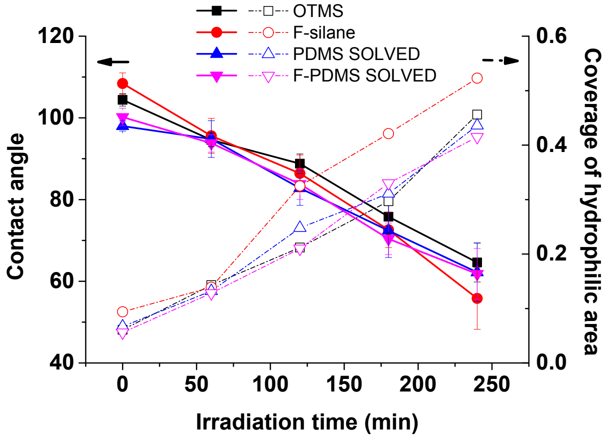


Figure 8S. Water contact angle and the corresponding coverage of hydrophilic area of OTMS SAMs and SOLVED coated ITO surfaces as function of UV exposure time.

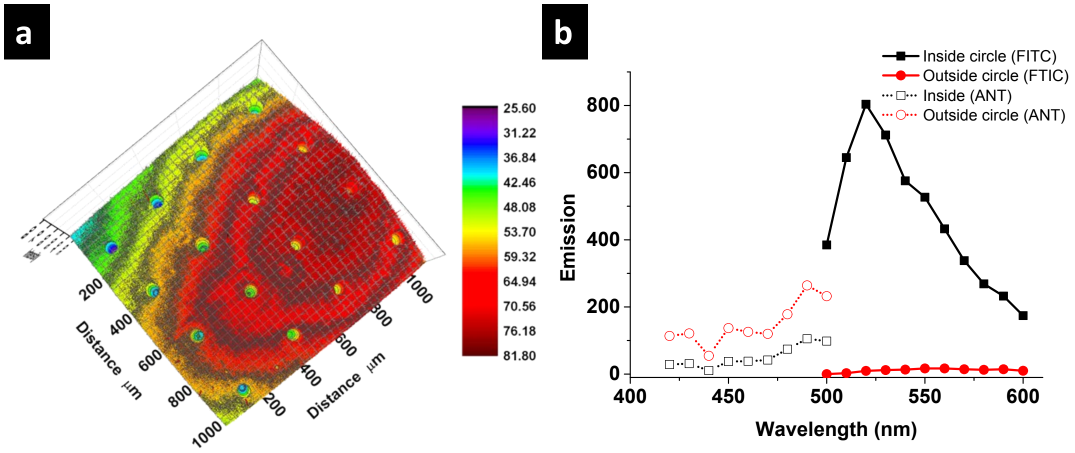


Figure 9S. (a) 3D surface plot for 9,10-Diphenylanthracene on the glass slide shown in Fig 4c. (b) Spectra for fluorescein and 9,10-Diphenylanthracene on a patterned PDMS SOLVED coated glass slide.

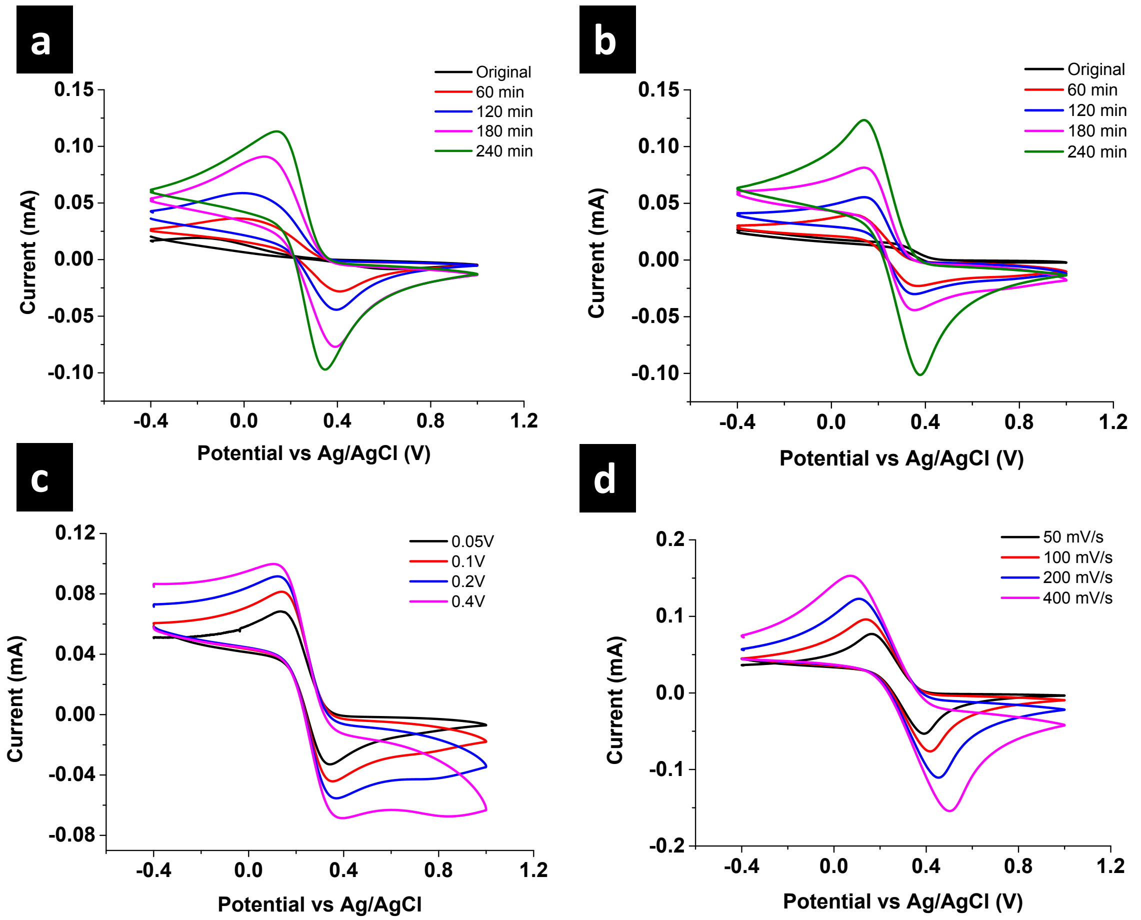


Figure 10S. The CVs for (a) OTMS and (b) PDMS SOLVED coated ITO with different UV exposure dose at scan rate of 0.1Vs^{-1}. (c) The CV for OTMS sample after 180 min UV exposure at different scan rates. (d) The CV for PDMS SOLVED sample after 180 min UV exposure at different scan rates.

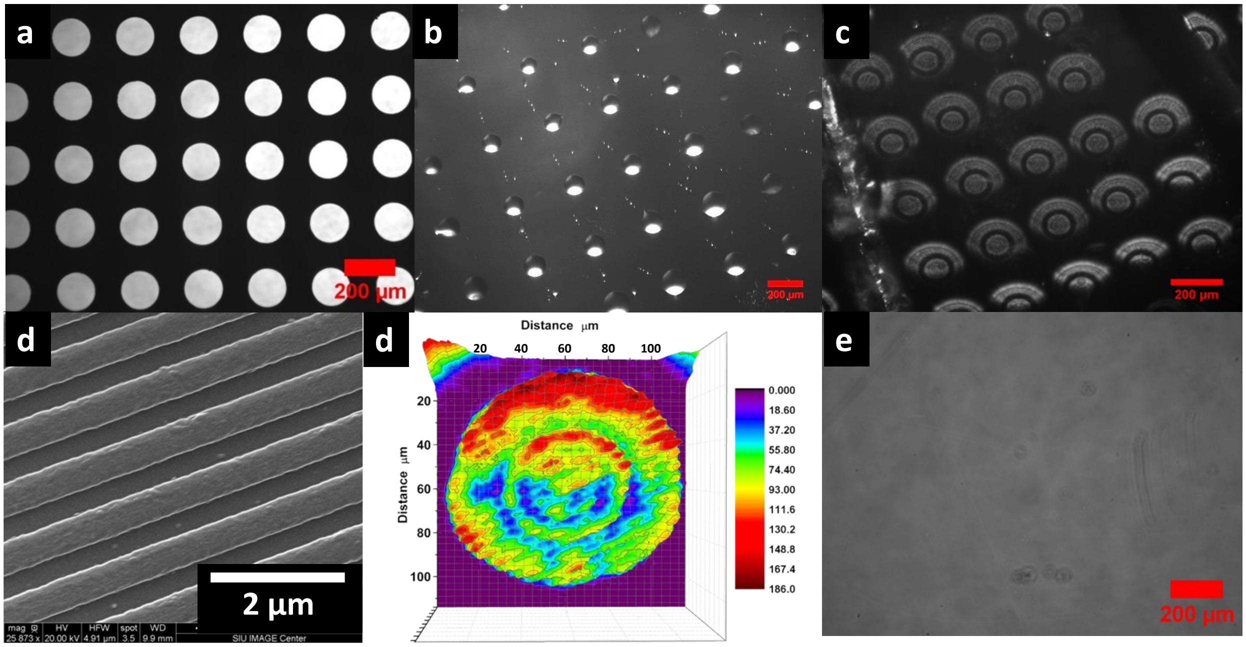


Figure 11S. (a) An optical micrograph of the mask used for patterning. (b) A resolved DVD image obtained using MLs array and 10x objective (NA=0.25). (c) Intensity plot of a resolved pattern. (d) Unresolved DVD pattern using 10X objective without aid of MLs.

Figure 11S shows that the DVD patterning was not resolved using a 10X objective (NA = 0.25) without the aid of $ZnCl_2$ ML because the diffraction limit of the microscope under these experiment conditions is 1080 nm which is much larger than pitch of the DVD (~640 nm).

General implications of the SOLVED for the surface functionalization and contamination, and the materials consideration for the SOLVED coatings.

Implications of the SOLVED to surface decoration. The temperature and molecular concentration of the source siloxane polymer at different zones along a heated oven with sample surface moving through it may allow control over surface functionality and deposition rate of the films on the surface. Unlike silane deposition which can be applied at lower temperatures, sometimes closer to room temperature, the SOLVED may require higher deposition and processing temperatures for the optimized surface coverage. These deposition parameters (temperature of the zone, speed of the conveyor belt, and the properties of the siloxane polymers for the coating) may limit the applications of the SOLVED coatings on the surfaces which must withstand higher temperature (>150 ^{o}C) during the SOLVED deposition.

Implication of the SOLVED films to siloxane contamination of the surfaces. It is important to consider the implication of siloxanes kept in close proximity to the surfaces. The SOLVED deposition on the surfaces is a thermally-activated process and occurs over a range of deposition temperatures when the surface is kept close to a siloxane polymer. Because the SOLVED is a vapor-phase deposition process, the siloxane coatings will form on the surfaces even when the siloxanes are separated from the surface. The surface contamination through the SOLVED process is not expected to be limited to glass surfaces but alumina, titania, polymers, and other surfaces may also potentially get contaminated through this route.

Material considerations for the SOLVED and SAMs coatings. The variety and range of functionality of commercially-available silanes are vast but limited functional commercially siloxane polymers are available (www.gelest.com). Finally, more studies are needed to optimize the SOLVED deposition parameters for siloxanes with different chemical functionalities.

Movie M1. An optical scanning video of DVD imaging using $ZnCl_2$ MLs array. The light was focused initially on the glass substrate where the MLs array was assembled. The focus was then moved along many imaging planes well-beyond the virtual image plane. The quality of resolution reached its best at the virtual geometric image plane and decreased away from this virtual plane. The dark rings (donate shape) observed in resolved patterns during imaging was shadow of our phase contrast filter which was projected on to the MLs.

Movie M2. Optical scanning of $ZnCl_2$ MLs array from side. We focused the light on the MLs in the row nearest to observer. It was then pushed further to show focusing of the MLs in other rows.

Movie M3. Dark-field optical scanning of the same MLs array showed in Movie *M2*. We use dark-field here that provided enhanced contrast.