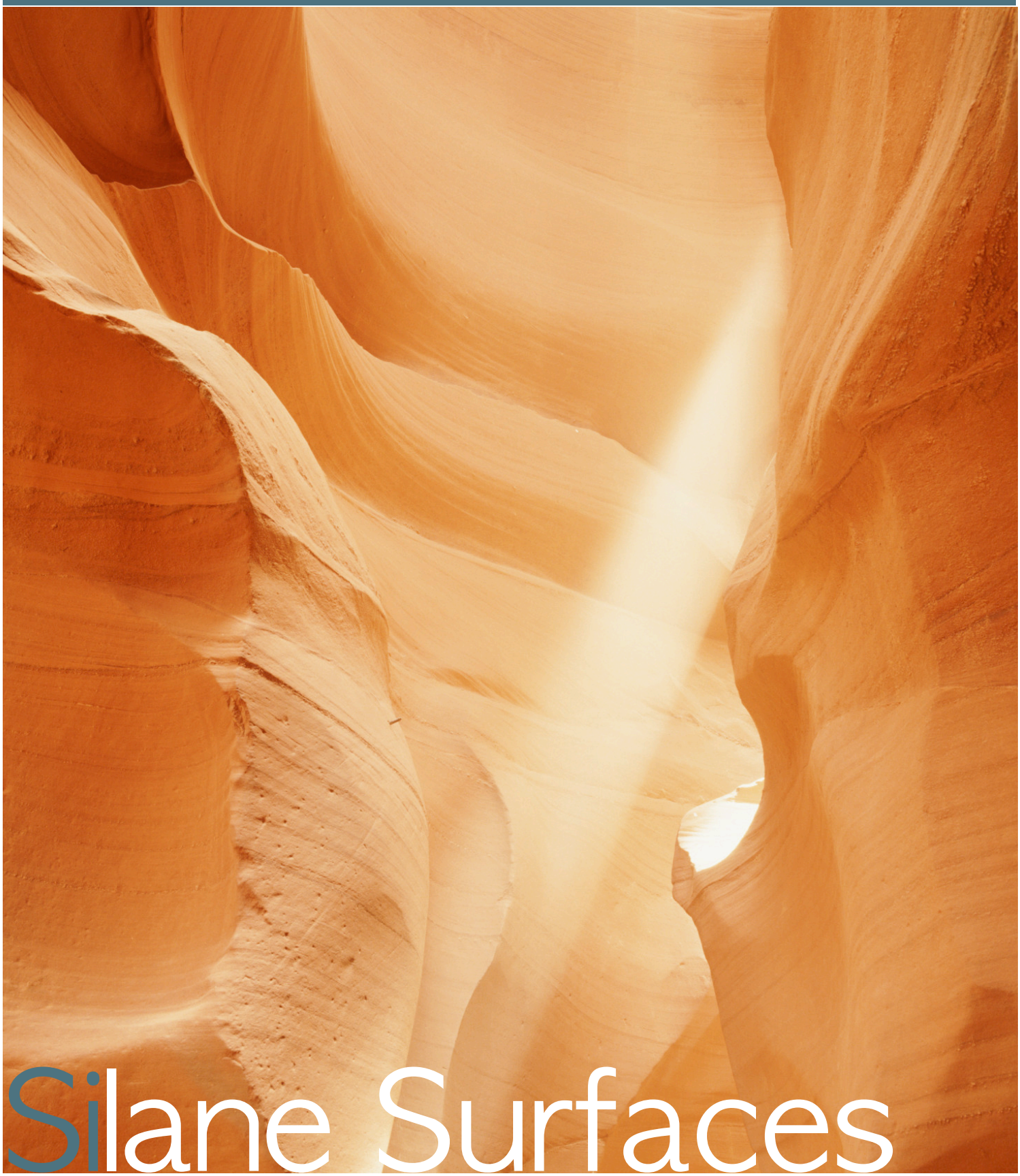
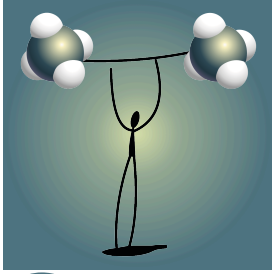
ProChimia Surfaces



Silane Surfaces Protocols

v.10.2011



ProChimia Surfaces

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Preface

The successful and reproducible deposition of a monolayer depends not only on temperature and hydration conditions but also on the type of silane used and the technique employed. Despite a significant amount of investigation into it and because of the great number of variables involved, the silanization process is neither fully understood nor highly reproducible. It is clear that achievement of optimal uniformity and reproducibility requires the surface cleansed of any contaminants with activated reactive hydroxyls group. There are numerous cleaning methods available in the literature. These include using various combinations of acids, bases, and organic solvents at different temperatures. Unfortunately, there is no universally accepted cleaning agent so far.

The cleaning of glass substrates

There are four most effective and reproducible methods available in the literature.

Procedure 1:
Initial cleaning of slides was done in 1:1 MeOH/HCl solution for 30 min with subsequent rinsing in copious amounts of deionized water. After rinsing, the slides were then dried under a stream of nitrogen immediately prior to silanization.

J.J. Cras, C.A. Rowe-Taitt, D.A. Nivens, F.S. Ligler, *Biosensors & Bioelectronics* 1999, *14*, 683-688.

Procedure 2:
Initial cleaning of slides was done in 1:1 MeOH/HCl solution for 30 min with subsequent rinsing in copious amounts of deionized water. After that, the slides were heated in concentrated H_2SO_4 for 2 h and then rinsed in deionized water. After rinsing, the slides were then dried under a stream of nitrogen immediately prior to silanization.

J.J. Cras, C.A. Rowe-Taitt, D.A. Nivens, F.S. Ligler, *Biosensors & Bioelectronics* 1999, *14*, 683-688.

Procedure 3:
Initial cleaning of slides was done in 1:1 MeOH/HCl solution for 30 min with subsequent rinsing in copious amounts of deionized water. After that, the slides were heated in concentrated H_2SO_4 for 2 h and then rinsed in deionized water and boiled in it for 30 min. After rinsing, the slides were then dried under a stream of nitrogen immediately prior to silanization.

A.V. Krasnoslobodtsev, S.N. Smirnov, *Langmuir*, 2002, *18*, 3181-3184.

Procedure 4:
The slides were heated at 80°C in NH_4OH (conc): H_2O_2 (30%): H_2O (1:1:5) mixture for 5 min and then rinsed in deionized water. After rinsing, the slides were then dried under a stream of nitrogen immediately prior to silanization.

J.J. Cras, C.A. Rowe-Taitt, D.A. Nivens, F.S. Ligler, *Biosensors & Bioelectronics* 1999, *14*, 683-688.

Cleaned, dried slides were placed in coplin jars for storage; slides stored longer than 24h were covered with methanol. Through these procedures and following cleaning, slides were handled with forceps to prevent the re-deposition of oils or contaminants on the surface.

These preparation procedures have proved to be effective; the slides were numerously recycled without noticeable deterioration, as confirmed by reproducible absorption spectra, and the above preparation procedures were found to be most effective in removing surface contaminants.

The cleaning and activation of silicone wafers

Procedure 1:
Silicon wafers were cleaned and hydroxylated in Piranha solution (mixture of 7:3 (v/v) 98% H_2SO_4 and 30% H_2O_2) at 90°C for 30 min. After that they were rinsed copiously by deionized water and dried under a stream of nitrogen immediately prior to silanization.

Caution ! **Piranha solutions react violently with organic materials and should not be stored in closed containers.**

S. Song, J. Zhou, M. Qu, S. Yang, J. Zhang, *Langmuir*, 2008, *24*, 105-109.

Procedure 2:
First, the silicon wafers were cut into pieces of approximately 15 mm × 15 mm. Then these substrates were cleaned and hydroxylated in Piranha solution (mixture of 1:1 (v/v) 98% H_2SO_4 and 27% H_2O_2) at room temperature for 20 min, then abundantly rinsed with deionized water. Wafers were dried by spinning with a spin-coater, then placed for 4 h at 70°C under vacuum.

Caution ! **Piranha solutions react violently with organic materials and should not be stored in closed containers.**

A. Pallandre, K. Glinel, A.M. Jonas, B. Nysten, *Nano Letters*, 2004, *4*, 365-371.

Procedure 3:
Silicon wafers surfaces were cleaned by immersion in 50:50 (v/v) H_2O_2 (30%)/NH_4OH (concentrated) for 30 min at room temperature and then rinsed thoroughly with deionized water. After the wafers were cleaned, surfaces were immersed in 5 vol % HCl (concentrated) for 60 min and then stored under water. Prior to silanization the surfaces were rinsed with water three times and dried with a jet of N_2.

Caution ! **The NH_4OH/H_2O_2 cleaning solution is extremely caustic and should be used with great care.**

G.A. Husseini, J. Peacock, A. Sathyapalan, L.W. Zilch, M.C. Asplunt, E.T. Sevy, M.R. Linford, *Langmuir*, 2003, *19*, 5169-5171.

Procedure 4:
First, the silicon wafers were cut into pieces of approximately 8 mm × 12 mm. Then these substrates were cleaned in a 2% Hellmanex solution in water for 90 min, sonicated for 5 min, rinsed with water, and dried with argon. For hydrophilization of the surface, the wafers were immersed in a mixture of NH_4OH (25%)/H_2O_2 (30%)(3:1 v/v) (20 mL), heated to 75 °C for 30 min, rinsed with water and dried with stream of argon.
Alkaline surfactant solution Hellmanex II was from Hellma, Müllheim, Germany.

Caution ! **The NH_4OH/H_2O_2 cleaning solution is extremely caustic and should be used with great care.**

C. Hoffmann, G.E.M. Tovar, *Journal of Colloid and Interface Science*, 2006, *295*, 427-435.

The silanization of the surface by trimethoxysilanes

Procedure 1:
Surface modification was accomplished by liquid phase deposition of silane in an organic solvent. All silanization steps were performed in a N_2-filled glove bag to minimize exposure to atmospheric water vapor. Cleaned slides were dried under nitrogen and were placed upright in Coplin jars in the glove bag. The slides were then incubated for 1h in a 2% solution of trimethoxysilane in dry toluene under nitrogen. Following three rinses of each slide in fresh toluene (to remove unbound silane), the slides were dried and stored under dry N_2. Contact angles on silanized slides should be determined within 24 h of cleaning and silanization.

J.J. Cras, C.A. Rowe-Taitt, D.A. Nivens, F.S. Ligler, *Biosensors & Bioelectronics* 1999, *14*, 683-688.

Procedure 2:
A 20 μL amount of trimethoxysilane was dissolved in 20 mL of a mixture of acetone and water. The ratio of acetone and water was 10:1 (by volume). Cleaned wafers were immersed in fresh silane solutions. After a certain period of time (2-24h), the wafers were removed from the solutions and sonicated for 5 min in acetone and 5 min in cyclohexane and rinsed by deionized water and dried with stream of nitrogen.

S. Song, J. Zhou, M. Qu, S. Yang, J. Zhang, *Langmuir*, 2008, *24*, 105-109.

Procedure 3:
The silanization of slides was performed using a 2% v/v acetone solution of a trimethoxysilane. In all cases, the slides were treated in the solution by complete immersion for a desired time (2-24h). At the end, silanized slides were washed in acetone, dried at ca. 100 °C on a hot plate for 5 min, and cooled for approximately 5 min.

A.V. Krasnoslobodtsev, S.N. Smirnov, *Langmuir*, 2002, *18*, 3181-3184.

Procedure 4:
Clean glass slides were immersed (2-24h) in the solutions of the trimethoxysilane in (95 : 5) ethanol : water mixture and adjusting the pH of the final solution to pH 2.0 with concentrated HCl. The concentration of trimethoxysilane was varied from 0.1 to 20 mg/ml. After dipping glass substrates into 4 ml of silane solution in test tubes (16 mm x 100 mm) for 2 h, the glass slides were sequentially rinsed with ethanol and water three times each. The washed slides were then dried overnight at 70°C. Each slide was then washed by soaking in 5 ml of 1% SDS solution overnight and washed thoroughly with deionized distilled water in an ultrasonic bath. After the reaction, treated surfaces were cured for 24 h at 70°C.

Alternatively, clean glass slides can be immersed in the solutions of the trimethoxysilane in anhydrous toluene overnight at 70°C. After that time, slides were sequentially rinsed with ethanol and water three times each. The washed slides were then dried overnight at 70°C. Each slide was then washed by soaking in 5 ml of 1% SDS solution overnight and washed thoroughly with deionized distilled water in an ultrasonic bath. After the reaction, treated surfaces were cured for 24 h at 70°C.

S. Jo, K. Park, *Biomaterials*, 2000, *21*, 605-616.

The silanization of the surface by dimethylchlorosilanes

Liquid phase deposition

Procedure 1:
The activated silicon wafers were transfered in PE reaction containers (Eppendorf, Hamburg, Germany) which were filled under argon flow with a mixture of 1.2 mL 10 mM dimethychlorosilane solution in dry toluene, containing 5 μL triethylamine as catalyst. The amount of water necessary for the hydrolysis of the chlorosilanes was adsorbed on the surface due to the hydrophilization procedure. The wafers in the silanization solutions were gently shaken for 30 min and then kept in the solution overnight. The silanized wafers were transferred in an oven, cured at 125°C for 2 h, and subsequently extracted with dichloromethane in a Soxhlet apparatus for 2 h to eliminate physisorbed silane. Then surface was rinsed three times with fresh toluene, dried and stored under dry N_2. The ellipsometric thickness and the contact angles of the silanized wafers were measured immediately after extraction.

C. Hoffmann, G.E.M. Tovar, *Journal of Colloid and Interface Science*, 2006, *295*, 427-435.

Procedure 2:
This method can be used only for dimethylchlorosilanes with low vapor pressure.
Silicon shards were placed in the recessed region (ca.1 mm deep) of a machined Teflon block. The appropriate dimethylchlorosilane (neat) was then placed on the surface of the silicon wafer, and the Teflon blocks containing the surface and reactive compound were placed in an oven (Thelco Laboratory Oven, Precision, Winchester, VA) at various temperatures (60-120°C) for 10 min to induce a reaction. The wafers were then removed from the oven, immediately rinsed with acetone to remove unreacted silane from the surface, and placed in a Soxhlet extractor (Chemglass, Vineland, NJ) overnight with m-xylene as the solvent.

Caution ! **This procedure should not be attempted above the flash point of a silane. Heated fumes from a volatile organic compound are potentially explosive.**

After cleaning in the Soxhlet extractor, the samples were rinsed with water, dried in a jet of N_2.
The ellipsometric thicknesses of silanized surfaces were the same whether they were cleaned by Soxhlet extraction or by a more simple procedure of rinsing with acetone, rinsing with water, rubbing with a soft artist's brush in the presence of aqueous 2% sodium dodecyl sulfate (SDS), and finally rinsing with water.

G.A. Husseini, J. Peacock, A. Sathyapalan, L.W. Zilch, M.C. Asplunt, E.T. Sevy, M.R. Linford, *Langmuir*, 2003, *19*, 5169-5171.

Gas phase deposition

Procedure 1:
A glass reactor was designed to conduct anhydrous gas phase silanization. It consists in a jacketed round bottom vessel, fitted with a cover with three feedthroughs with poly(tetrafluoroethylene) stopcocks (gas inlet and vacuum outlet). A third, unstoppered, feedthrough was used to record temperature. A Viton® seal was used to seal the reactor. A fourth stoppered inlet, directly connected to the side of the reactor, allowed to inject the silane directly at the bottom of the reactor. The temperature in the reactor was controlled by flowing silicone oil through the jacket. Before any silanization, all glassware was cleaned by immersion for 16h in KOH-saturated isopropanol bath, and rinsed thoroughly with water. The closed reactor was then dried at 100°C for 12 h under continuous pumping (primary vacuum ensured by a rotary pump fitted with a liquid nitrogen cold trap). After introduction of dry argon, about 12 freshly cleaned silicon wafers were placed over a two-stories glass tray fitted with an upper cover protecting samples from contamination resulting from silane condensation on the reactor cover, and introduced in the reactor. The samples and reactor were annealed at 70°C for 4h under primary vacuum. Dry ultra-pure argon was then introduced and the silane was injected. The reaction was allowed to proceed for 24h in a slight over pressure of dry argon. After 24h, the reactor was pumped until complete removal of remaining traces of silane, opened in a flow of dry argon. The silanized wafers were washed in a Soxhlet with chloroform for 24h, washed three times with fresh chloroform and dried with a stream of argon.

A. Pallandre, K. Glinel, A.M. Jonas, B. Nysten, *Nano Letters*, 2004, *4*, 365-371.

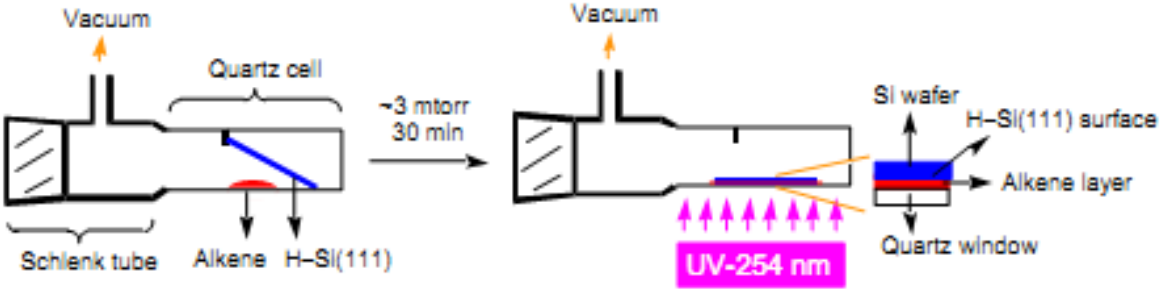
Photo-induced Surface Hydrosilylation

Procedure 1:
The apparatus was prepared by fusion of the open end of a five-side-polished quartz cell with the open bottom of a Schlenk tube (Figure 1). It was cleaned with Piranha solution (H_2SO_4/30% H_2O_2 3:1) at 80°C for 30 min, washed thoroughly with Millipore water, covered with aluminum foil and dried in a clean oven at 150°C.

Caution ! **Piranha solutions react violently with organic materials and should not be stored in closed containers. Care must be taken while handling Piranha solutions**

A single side polished and (111) oriented silicon wafers were cut into pieces of ca. 1x1 cm^2, cleaned with Piranha solution (H_2SO_4/30% H_2O_2 3:1) at 80 °C for 30 min, thoroughly washed with Millipore water, etched in 10% buffer-HF (Transene) for 5 min and then in 40% NH_4F for 15 min under N_2 purge, and dried immediately with a flow of nitrogen. The substrate was immediately placed inside a freshly cleaned and dried quartz cell, and tilted with the polished H−Si (111) surface facing downward (Figure 1).

Figure 1 Experimental Setup of Photo-induced Hydrosilylation on H-Si (111) Surfaces



A droplet (~1-3 mg) of the alkene in a pipette was carefully placed on the quartz window below the wafer but without touching it. After the cell was degassed at ~10-4 mbar for 30 min, the substrate was allowed to fall down (by lightly tapping the cell) onto the droplet, forming a thin and homogeneous layer between the H–Si (111) surface and the quartz wall (Figure 1). The H–Si (111) surface was illuminated for 30 min with a hand-hold 254 nm UV-lamp (Model UVLS-28, UVP) placed ~1 cm away from the cell. The sample was taken out and washed sequentially with petroleum ether, ethanol, and dichloromethane, followed by drying with a stream of N_2 gas.

C.M. Yam, J.M. Lopez-Romero, J. Gu, C. Cai, *Chemical Communications*, 2004, 2510-2511.