

# Nanoscale hydrophobic coatings for the separation of liquid mixtures

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## ABSTRACT

Organofunctional silane containing coatings are widely used to modify surface chemistry and have many applications in micro- and nanofluidics because liquid motion on these scales is strongly influenced by capillary or wall effects. In this work we focus on the development of nanoscale coatings for chemically patterned surfaces using fluorosilane SAMs and fluorine containing methacrylate coatings for the novel approach to separate emulsions on surfaces with an abrupt change of wettability from hydrophilic to hydrophobic. As a model system we investigate the separation of Toluene- Water- emulsions on such surfaces and thus aim for coatings easy to apply resulting in contact angles bigger  $90^\circ$  the same time being solvent resistant. We study the fastness to solvents (Toluene and Acetone) as a function of the deposition parameters and demonstrate emulsion separation. The fluorosilane SAMs are patterned by combining CVD and UV-lithography while the methacrylate coatings are deposited by dipcoating.

**Keywords:** Surfaces and Films, Separation, Surface Characterization, Nano Structured Material Applications

## 1 INTRODUCTION

Organofunctional nanoscale silane coatings are widely used to modify surface chemistry. A famous example are self-assembled monolayers (SAM) where monomolecular densely packed layers of silanes are used to tune surface energy [1]. Fluorosilane SAMs can be used to obtain even ultrahydrophobic surfaces [2]. As well silane containing side chains can be applied as crosslinking agents for ultrahydrophobic methacrylate coatings on aluminum oxide [3]. Such coatings have many applications in micro- and nanofluidics because liquid motion on these scales is strongly influenced by capillary or wall effects. In microfluidic systems differences of wettability on chemically patterned surfaces allow to drive liquid in case of a surface energy gradient [4] and to guide liquid in case of abrupt surface energy change [5]. Recently our co-workers reported the possibility to separate mixtures of incompatible liquids on surfaces with surface energy gradients [6]. In this work we focus on the development of nanoscale chemically patterned surfaces using fluorosilane SAMs and fluorine containing methacrylate coatings for the novel and more simple approach to separate incompatible

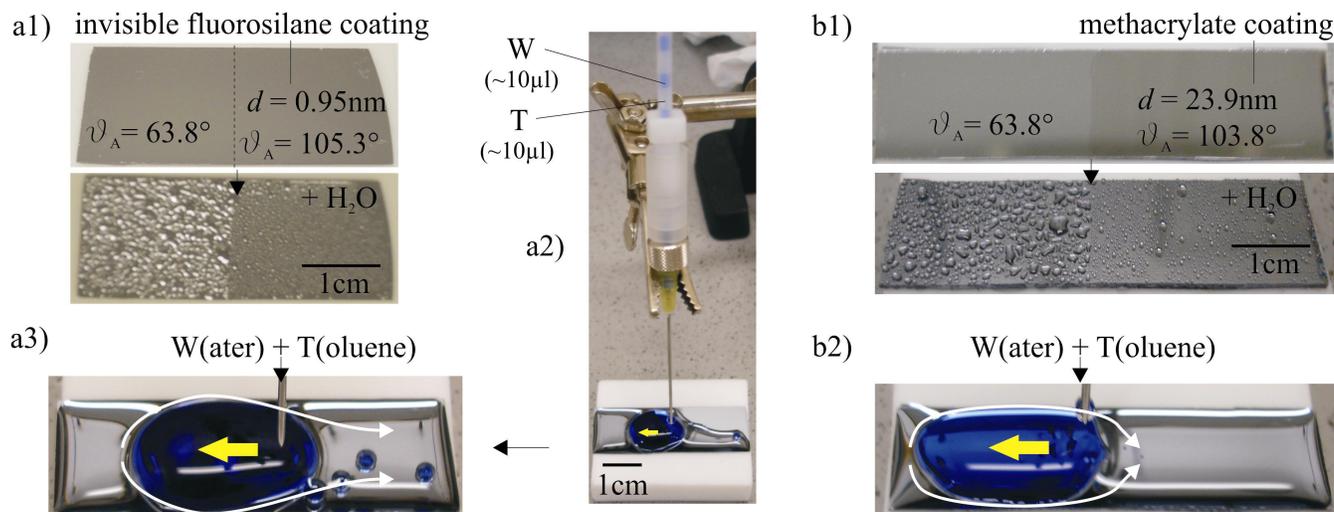


Figure 1: a1) Silicon substrates half covered with hydrophobic fluorosilane SAMs of thickness  $d$  and adv. contact angle  $\theta$  are used for a2) the separation of Toluene/water mixtures/beads. a3) Due to the internal Laplace pressure difference on the hydrophobic/-philic interface water drops are driven to the hydrophilic side and merge the same time pushing the Toluene away. b1, b2) Analogous experiment with dipcoated methacrylate coatings on silicon substrates.

liquid mixtures on surfaces with an abrupt change of wettability from hydrophilic to hydrophobic where the hydrophilic side is given by the native oxide surface of a silicon substrate (Fig.1).

We aim for hydrophobic nanoscale surface coatings easy to apply resulting in contact angles bigger  $90^\circ$  the same time being solvent resistant. For the first experiments we milled the separation cell into bulk teflon with a cavity into which epoxy resin has been introduced. To allow further miniaturization and for applications as sensor coatings in this work we investigate two approaches to obtain chemically patterned surfaces for separation. Firstly we selectively deposit a fluorosilane by combining UV-lithography and chemical vapor deposition (CVD). Secondly we pattern the silicon substrates by the selective deposition of hydrophobic methacrylate films using dip coating. In both cases the film thickness is characterized by ellipsometry and the surface energy is determined by contact angle measurements. All samples used are previously cleaned in a mixture of  $\text{NH}_4\text{OH}$ (28-30%):  $\text{H}_2\text{O}_2$ (35%):  $\text{H}_2\text{O}$ = 1: 1: 4 at  $85^\circ\text{C}$ .

## 2 RESULTS AND DISCUSSION

### 2.1 Fluorosilane SAMs

Preparation: 1) Photoresist is spincoated at 3000rpm for 30s onto the silicon substrates and dried at  $100^\circ\text{C}$  for 20 minutes. Subsequently the resist is exposed to UV light using a UV blocking foil as a mask resulting in pattern formation after development in alkaline solution. 2) Tridecafluoro-1,1,2,2-Tetrahydrooctyldimethylchlorosilane as obtained from the manufacturer is transferred in a water-free argon atmosphere (glove box) to a syringe for further processing under ambient conditions. Several drops are added to the petry dish into which the silicon substrates with patterned photoresist are placed. The CVD is carried out at  $70^\circ\text{C}$  in the oven. After deposition the photoresist is

removed with Acetone in an ultrasonic bath resulting in a selectively coated silicon substrate.

Results: A hydrophobic fluorosilane SAM is formed on the surface previously not covered by photoresist. The layer thickness increase with increasing deposition time from 2 hours to 4 hours while the layers become thinner again for 5 hours and 6 hours (Fig.2a). As a monochlorosilane is used no crosslinking between individual fluorosilane molecules attached to the surface can occur. Thus the increase in layer thickness with increasing deposition time from 2 hours to 4 hours is due to a densification and possible rearrangement of the fluorosilane layer. The thinning effect after 4 hours has been observed repeatedly. We suspect that this is due to a reordering of the layer occurs while more fluorosilane is attached. This presumption is supported by the fact that the advancing contact angle increases continuously from 2 hours to 6 hours (Fig.2b). For the receding contact angle no clear trend can be observed but still the data supports to propose that the receding contact angle remains constant taking into account a measurement error of approximately  $1^\circ$  (Fig.2b). Increasing contact angle hysteresis together with constant receding contact angles points to no significant increase in defect density but an increase of the silane layer hydrophobicity itself which would be as well in agreement with a reordering process.

### 2.2 Methacrylate Coatings

Preparation: 1) The silicon samples are dipped into a Toluene solution containing Poly-(t-butylmethacrylate-co-Zonyl<sup>TM</sup>-co-3-trimethoxysilylpropylmethacrylate) 6:2:2. Concentrations are varied from 0.1% to 1%. The dip coating speed is varied from 0.3mm/s to 1.5mm/s. 2) Afterwards the layers are tempered in water vapor atmosphere at  $120^\circ\text{C}$  for 2 hours in the oven and rinsed with water.

Results: Both concentration and dip coating speed determine the layer thickness of the hydrophobic coating

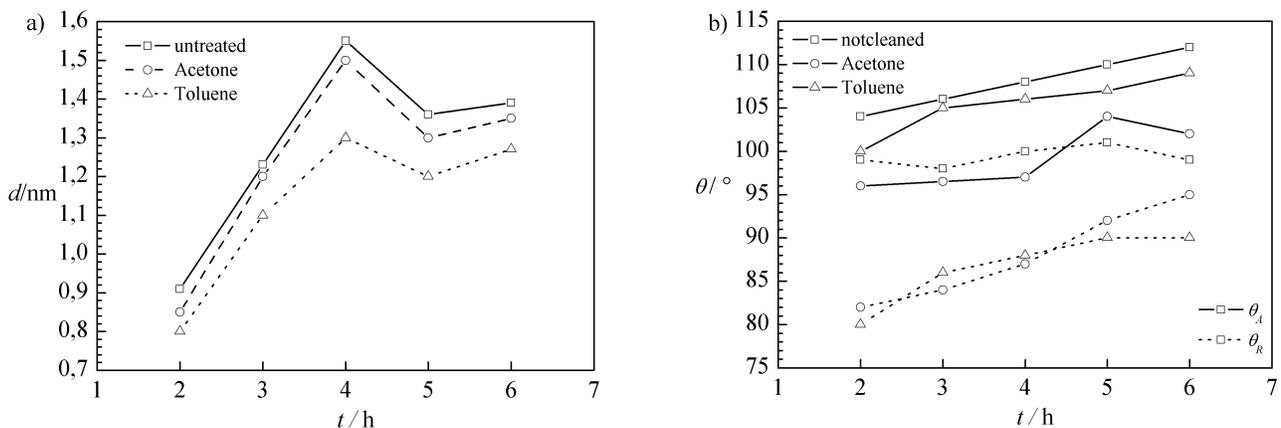


Figure 2: Fluorosilane SAMs. Characterization of untreated samples and samples after exposition either to Acetone or Toluene at  $65^\circ\text{C}$  in the ultrasonic bath. a) layer thickness  $d$  versus CVD-time  $t$ , error  $\pm 0.1\text{nm}$ . b) advancing and receding contact angle versus CVD-time  $t$ , error  $\pm 1^\circ$ .

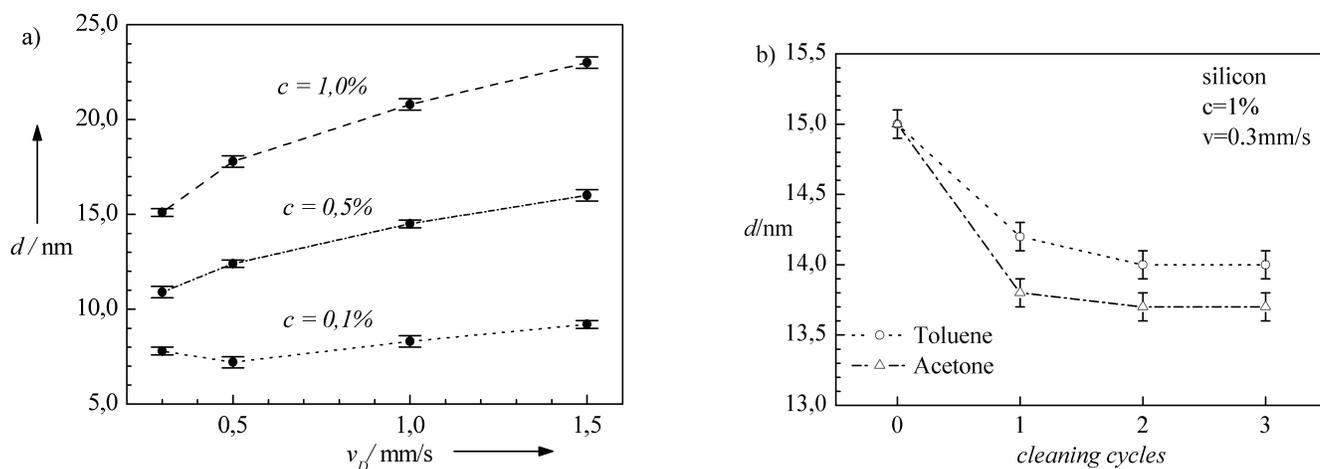


Figure 3: Hydrophobic Methacrylate Coatings. Layer thickness of untreated samples and impact of exposition to Acetone or Toluene at 65°C in the ultrasonic bath. (no significant change of advancing and receding contact angles:  $95^\circ < \theta < 104^\circ$ ) a) layer thickness  $d$  as a function of polymer concentration  $c$  and dip coating speed  $v_D$  b) layer thickness  $d$  after multiple expositions either to Acetone or Toluene at 65°C in the ultrasonic bath.

which can be varied from 7nm to 23nm (Fig.3a). Both an increase of polymer concentration or dip coating speed result in an increase of the layer thickness. Advancing and receding contact angle are independent of the layer thickness because the surface properties namely the number of fluorinated groups per unit area doesn't depend on the film thickness.

### 2.3 Solvent Resistance

To check the chemical stability of the nanocoatings we investigate the solvent resistance by exposing the modified silicon substrates for 30min either to boiling Acetone or to heated Toluene in an Ultrasonic bath at 65°C. In case of the fluorosilane SAMs we find that the general trend which is an increase of thickness, receding and advancing contact angle with increasing deposition time is preserved but still changes occur: In both cases the layer thickness is decreased (Fig.2a). The thickness decrease is significantly stronger in the case of Toluene but surprisingly the advancing contact angle remains bigger than after Acetone exposition (Fig.2b). The receding contact angle is reduced in both cases but approaches the same magnitudes (Fig.2b). In case of the methacrylate coatings the solvent treatment is repeated three times (Fig.3b). We find that the layer thickness decreases with increasing number of cleaning cycles approaching a fixed value while advancing and receding contact angle remain unaffected. We assume that this is due to a wash out of uncrosslinked material. Uncrosslinked material may exist because the water vapor temper process mainly affects surface near layers. This is supported by the fact that advancing and receding contact angle which are measured at the surface remain constant. Furthermore samples dip coated by hand with significantly thicker layers in the micron regime are not solvent resistant even after carrying out the temper process. This

demonstrates that here chemical stability benefits from down scaling film thickness. To sum up we find that the hydrophobicity as the property of interest is preserved to a large extend after exposure to solvents for both types of coatings.

Finally we demonstrate the possibility of separating Toluene-Water-mixtures on such surfaces with an abrupt change of surface energy from hydrophilic to hydrophobic (Fig.1). The separation process is based on the fact that water with a surface tension of 72.8 dyne/cm preferably wets the hydrophilic side while Toluene has just a weak preference of the hydrophilic side due to a lower surface tension of 28.5 dyne/cm. As the water wets the surface more and more the Toluene is forced to flow to the hydrophobic side. The separation has been successfully carried out with the following surface material combinations and contact angles: Epoxy Resin,  $78^\circ < \theta < 83^\circ$ / Teflon,  $90^\circ < \theta < 95^\circ$  (bulk);  $\text{SiO}_2$ ,  $21^\circ < \theta < 64^\circ$ / Fluorosilane SAM,  $98^\circ < \theta < 110^\circ$  (as described above);  $\text{SiO}_2$ ,  $21^\circ < \theta < 64^\circ$ / Methacrylate-CP  $95^\circ < \theta < 104^\circ$  (as described above). The dynamics of this process is discussed in detail elsewhere [7].

## 3 CONCLUSION

In conclusion we have established three methods (including the Teflon-epoxy-approach) for the fabrication of chemically patterned surfaces which all are suitable for the separation of incompatible liquid mixtures. Each method provides specific advantages which are summarized in Tab.1.

For the fabrication of single mm-scale robust devices which are often used for testing the Teflon-epoxy-approach seems to be most favorable especially with respect to the fact that conventional macroscopic fluidic components easily can be integrated. If microscale devices are required

<b>material, method</b>	<b>pattern dimension</b>	<b>size</b>	<b>chemical stability</b>	<b>mechanical stability</b>	<b>fabrication</b>
fluorosilane nanofilm, CVD and photolithography	2-dim.	++	+	-	+
methacrylate nanofilm, dip coating	3-dim.	+	+	-	+
teflon-epoxy, casting and milling	3-dim.	-	++	++	-

Table 1

both nanofilm approaches are applicable. Here the choice is between complex 2-dimensional patterns in the case of the fluorosilane nanofilm or more simple but 3-dimensional patterns in the case of the methacrylate nanofilm. Due to there nanoscale thickness both surface types may be combined with surface sensitive devices like FET. Thus based on these investigations we can provide suitable patterning methods for a wide range of applications.

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