

# Chemical vapour deposition of octadecyltrichlorosilane on plasma activated surfaces of silicon atomic force microscopy probes

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**Abstract:** Deposition of octadecyltrichlorosilane (OTS) layers is commonly used in electronic industry and in various applications that require modification of silicon surfaces as in biosensors, actuators or atomic force microscopy. Usually, OTS functionalization of silicon surfaces is based on wet chemistry techniques comprising self-assembled monolayers (SAMs) deposition of OTS from solutions on silicon surfaces that were activated (cleaned and hydroxylated) in piranha solution. However, this technique may yield inhomogeneous depositions characterized by formation of nanoscopic OTS particulate aggregates on the functionalized surfaces due to polymerization of OTS molecules on water contaminated surfaces. Therefore control of water contaminant is critical to OTS functionalization of silica surfaces. In this work we use low-pressure plasma of a luminescent discharge in air and water vapour to clean and hydroxylate silicon surfaces of AFM probes and, then, chemical vapour deposition of OTS on the activated surfaces. The whole process takes place in the same chamber at low pressure, which reduces considerably the surface contamination during the process. However, we have found that in this particular technique, the intentional introduction of certain amount of water vapour in the deposition chamber is beneficial to OTS depositions. There is an optimum in the amount of water introduced into the deposition chamber, introduction of too much water leading in formation of particulate aggregates of OTS, while introduction of a too small quantity of water results in formation of ill-covered OTS surfaces. The OTS covered surfaces were characterized by water contact angle measurements and AFM investigations of OTS surface topography. Depositions on silicon AFM probes were characterized by adhesion and friction force measurements.

**Keywords:** plasma-activated surface, low-pressure discharge plasma, chemical vapour deposition, octadecyltrichlorosilane functionalization, atomic force microscopy probes

## 1. Introduction

Self-assembled monolayer (SAM) deposition of organosilane molecules (silanization) has been widely used to design specific surface properties (physical and chemical) of glass, quartz and Si wafers [1, 2]. The silane modified surfaces have found important applications in the fields of electronics, adhesion, corrosion inhibition, etc [3]. The SAM deposition of organosilanes such as octadecyltrichlorosilane (OTS,  $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ ) is a complicated technique, with multiple steps of hydrolysis, cross-linking and silanization [4]. The two most important techniques used for silanization of silica surfaces are SAM deposition in liquid solutions and chemical vapour deposition (CVD). The SAM deposition in liquid solutions is considered a simple method and is well documented [5, 6]. The CVD holds better flexibility, but the technique requires expensive vacuum equipment [5]. Both deposition techniques were successfully used to fabricate ordered and densely packed SAM of silane molecules on Si substrate [7, 8].

In the present work, we use low-pressure plasma of a luminescent discharge in water-saturated air to clean and hydroxylate silicon surfaces of AFM probes and, then, CVD of OTS on the plasma activated surfaces. This deposition method has the advantages of reduced surface contamination due to use of low-pressure plasma surface activation and in situ CVD (plasma activation and CVD in OTS vapour taking place in the same chamber). However, we have found that in this particular technique, the intentional introduction of certain amount of water vapour in the deposition chamber, prior of CVD, is beneficial to OTS film depositions. There is an optimum

in the amount of water introduced into the deposition chamber, introduction of too much water leading in formation of particulate aggregates of OTS, while introduction of a too small quantity of water leads to formation of ill-covered OTS surfaces. The quality of OTS functionalized surfaces is assessed by atomic force microscopy (AFM) investigation of surface topography and water contact angle measurements. Also, the deposition on the silicon AFM probes is characterized by adhesion and friction force measurements.

## 2. Experiment

Octadecyltrichlorosilane ( $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ , OTS, > 90%) and ethanol (> 99.8%) were purchased from Sigma-Aldrich and used as received. Distillate water was freshly purified and deionised using an Ultrapure Academic Milli-Q system. Before OTS deposition, the silicon AFM probes and polished silicon wafers were cleaned with ethanol and distillate water and then dried. The topography images of the OTS modified surfaces were obtained by AFM scans in tapping mode using a silicon probe (HQ:NSC35/No Al from Micromasch) with the nominal resonance frequency and tip curvature radius of 150 kHz and 8 nm, respectively.

The plasma activation (cleaning and hydroxylation) of surfaces of silicon substrates and OTS CVD were performed in the same reactor (see **Fig. 1**). Plasma surface treatment was done in negative glow plasma of a d.c. luminescent discharge in air and water vapour mixture at low pressure. The silicon substrates were loaded on small stainless steel cathode (disk with diameter of 4 cm) and the chamber was vacuumed down to  $10^{-2}$  Torr for about

30 minutes. Then, water-saturated air was introduced in discharge chamber at pressure of 0.3 Torr and the d.c discharge was kept on (voltage around 380V and current intensity around 5 mA) during 2 minutes. During this step, the surfaces of silicon substrates were cleaned by chemical etching of contaminant organic molecules and hydroxylated by reactive oxygen species generated in plasma of air and water vapour mixture [9]. After the hydroxylation process, a certain amount of water vapour was intently introduced in the deposition chamber by raising the pressure of water-saturated air (1-10 Torr) and maintaining this pressure for time periods varying from 1 minute to 4 minutes. Then, the reactor chamber was vacuumed to the ground pressure ( $10^{-2}$  Torr) and OTS vapour was introduced for CVD. The pressure of OTS vapour introduced in the reactor chamber was controlled by the temperature of OTS liquid reservoir (80°C) connected to the discharge chamber by a special inlet Teflon tube that dispersed the OTS vapour above plasma activated silicon surface (Fig. 1).

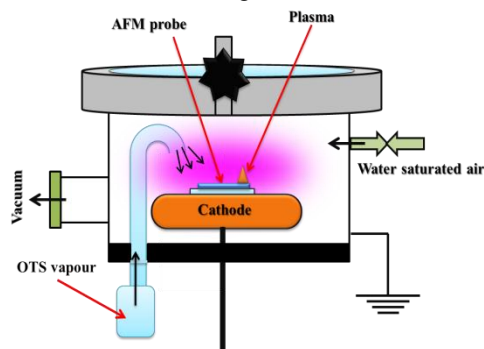


Fig. 1. Schematic representation of the plasma reactor setup used for plasma surface activation and OTS CVD.

The deposition in OTS vapour was done at room temperature for time intervals ranged from 2 hours to 24 hours. After the deposition, the discharge chamber was vented and the OTS covered silicon substrates (silicon AFM probes or polished silicon wafers) were transferred to an oven, where they were baked at 100°C in ambient air for 24 hours. This process favours the self-organisation of OTS molecules on silicon surfaces. The freshly prepared samples were stored in medium vacuum until their use in AFM measurements.

### 3. Results

To obtain an optimal OTS deposition by the technique described above we have varied a number of deposition parameters, i.e. duration of plasma treatment, duration of OTS CVD, the pressure of OTS vapour in CVD and the amount of water introduced in the reactor between plasma surface activation and CVD steps (by changing the partial pressure of water vapour and exposure time of activated surfaces to water vapour). We have noticed that 2 minutes of plasma treatment is enough to render silicon surfaces clean and densely hydroxylated. The temperature of OTS

reservoir was raised to maximum 80 °C. Values above 80°C were not used in order to avoid oxidation of OTS in the medium vacuum of the reactor. At the partial pressure of OTS vapour determined by this value of the OTS reservoir temperature, the minimum deposition time for a good OTS coverage in CVD was determined to about 24 h. This minimum value of the OTS CVD time was determined based on observation of OTS surface topography and rise of water contact angle values with the deposition time (the value of water contact angle was approximately 98° after 24 hours of OTS CVD). The morphology of OTS modified surfaces of AFM probes was characterized with an atomic force microscope (XE 70 system from Park Systems, South Korea) working in tapping mode. The AFM topography images of AFM probe were analysed to determine the RMS value of the roughness. In the following experiments, we set the time deposition to 24 hours and the temperature of OTS reservoir to 80°C and varied the time of surface exposure to water vapour from 1 minute to 4 minutes (the partial pressure of water vapour being constant,  $p_{\text{water}} = 0.26$  Torr). The AFM topography image of the OTS surface obtained for these process parameter values for 1 minute of surface exposure to water vapour is presented in Fig. 2. The OTS surface obtained by chemical vapour deposition is smooth but presents uniformly distributed small (around 10 nm in height) aggregates of polymerized OTS molecules. One of the explanations of presence of these aggregates can be the excessive amount of water condensed on plasma activated silicon surface during its exposure to water vapour. During this exposure time water is absorbed on hydroxylated surface and form small sessile nanodroplets. These sessile water nanodroplets are places for polymerization of OTS molecules to form small aggregates.

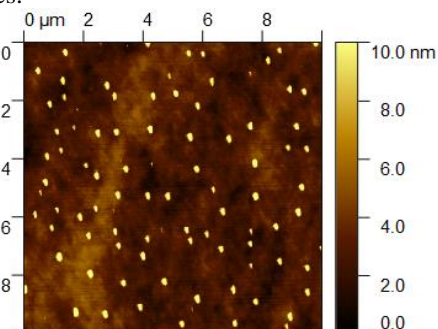


Fig. 2. AFM topography image (10 µm × 10 µm) of the OTS modified surface prepared by chemical vapour deposition (CVD deposition time = 24 hours,  $p_{\text{water}} = 0.26$  Torr, surface exposure time to water vapour = 1min.).

Increase of surface exposure time to water vapour determined formation of larger water nanodroplets on the hydroxylated silicon surfaces, which determined polymerization of larger OTS aggregates (height order of several tens of nanometres) as one can observe in Fig.3. The size (volume) of OTS aggregates increases with the

increase of duration of surface exposure to water vapour. Therefore, we have concluded that the water vapour pressure of 0.26 Torr and is too large.

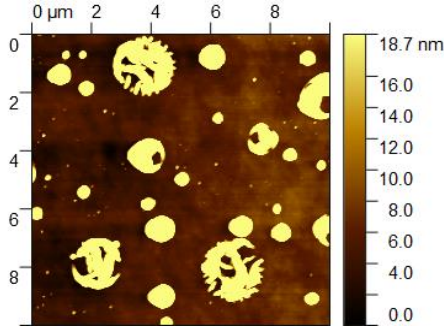


Fig. 3. Topography AFM image (10  $\mu\text{m} \times 10 \mu\text{m}$ ) of the OTS modified surface prepared by chemical vapour deposition ( $p_{\text{water}} = 0.26 \text{ Torr}$ , surface exposure time to water vapour = 2 min,  $t_{\text{dep}} = 24 \text{ hours}$ ).

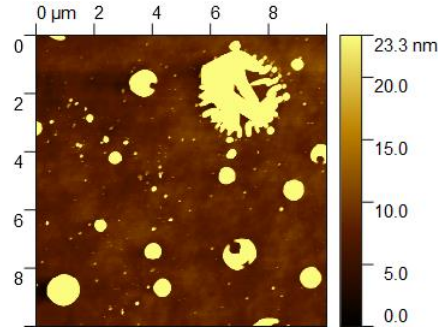


Fig. 4. Topography AFM image (10  $\mu\text{m} \times 10 \mu\text{m}$ ) of the OTS modified surface prepared by chemical vapour deposition ( $p_{\text{water}} = 0.26 \text{ Torr}$ , surface exposure time to water vapour = 4 min,  $t_{\text{dep}} = 24 \text{ hours}$ ).

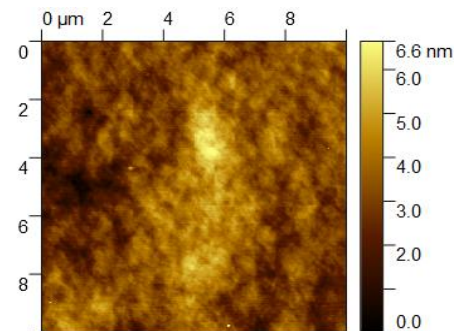


Fig. 5. Topography AFM image (10  $\mu\text{m} \times 10 \mu\text{m}$ ) of the OTS modified surface prepared by chemical vapour deposition ( $p_{\text{water}} = 0.02 \text{ Torr}$ , action time = 1 min,  $t_{\text{dep}} = 24 \text{ hours}$ ).

To prevent the OTS polymerization in large or small aggregates, we reduced the partial pressure of water vapour to  $p_{\text{water}} = 0.02 \text{ Torr}$  [10] and exposed the plasma activated silicon surface to water vapour for 1 minute. In

this case, according to the topography image presented in **Fig. 5**, the OTS thin film is compact and homogeneous (one can notice the absence of aggregates). Another indicator of a compact and homogeneous molecular thin film is given by the large value of the water contact angle of the OTS surface (approximately  $103^\circ$  in this case). To probe the quality of OTS functionalization of the surface of AFM probes, we performed force spectroscopy measurements in ambient air (RH = 40%) on glass samples with AFM probes before and after their functionalization. These investigations were done by acquisition and analysis of force-distance curves taken in force spectroscopy measurements performed on arrays of  $8 \times 8$  positions homogeneously distributed on an area of  $1 \mu\text{m} \times 1 \mu\text{m}$  of glass surface. Each force curve was performed with a vertical displacement speed of the AFM probe of  $1 \mu\text{m/s}$ . Typical force-versus-distance curves obtained with an AFM probe (HQ:NSC35/No Al from Micromasch) before and after OTS functionalization are presented in **Fig. 6** and **Fig. 7**, respectively

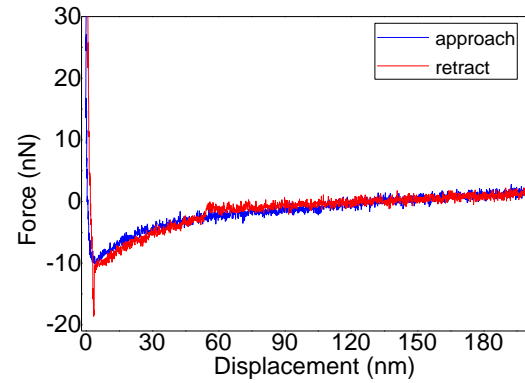


Fig.6. Typical force-distance curve for the interaction between a silicon AFM tip and a glass substrate (AFM probe before functionalization).

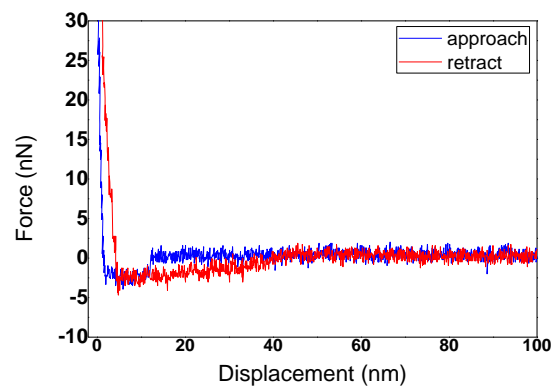


Fig.7. Typical force-distance curve for interaction between OTS-functionalized AFM tip and a glass substrate (AFM probe after OTS functionalization).

The force-distance curves acquired in ambient air with silicon AFM probe before functionalization showed a typical variation characteristic to formation (on the approach curve) and elongation and rupture (on the retract curve) of a capillary water bridge formed at the contact between hydrophilic surfaces of the sharp silicon AFM tip and flat silica sample [11]. Values of about 10 nN for the adhesive force and of 50 nm for the elongation length for the capillary water bridge formed at tip-sample contact are observed. The force-displacement curves obtained for OTS functionalized AFM tip on glass samples in ambient air show a much smaller adhesion force (about 3 nN) and a smaller elongation length (about 40 nm) of the water capillary bridge formed at tip-sample contact. This is a clear effect of hydrophobic surface of the OTS covered AFM tip.

#### 4. Conclusion

High quality OTS functionalization of silica surfaces was achieved by combining plasma surface activation and chemical vapour deposition technique in the same reactor. The whole process is completely dry (does not use solvents) and have the advantage of avoiding contamination by completing activation and silanization in the same chamber. The quality of silanization process was assessed by analysis of atomic force microscopy images of the silane (OTS) modified silica surfaces, water contact measurements and AFM force spectroscopy measurements performed with OTS functionalized AFM probes. An additional fabrication step consisting in intent exposure of plasma activated surface to water vapour was introduced to favour silanization reaction of OTS molecules with plasma-hydroxylated silica surfaces. It is proven here that this additional fabrication step plays a crucial role in formation of a homogeneous film of OTS molecules on the silicon surfaces. At height values of water vapour pressure, the water molecules condense on the substrate in nanodroplets, creating in this way nanometric aggregates of polymerized OTS. The size and density of OTS aggregates is determined by the amount of water condensed on the surface. At low water vapour pressures and short exposure time, the water molecule no longer condenses in drops, but forms a thin and uniform layer at the interface with the substrate. In this case, the OTS molecules are attached one by one on the water layer, resulting in formation of a uniform and compact OTS film.

#### 5. References

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