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Contact Angle Measurements on Thin Films

Abstract:

In P03 beamline at PETRA III a “DataPhysics OCA35” contact angle machine has been recently bought in order to perform fast and cost-less quality control tests on samples prepared in the laboratories. This technique allows investigating the structure of surfaces using its hydrophilicity properties. In this report some measurements aimed to verify the effect of acid and plasma cleaning on silicon surfaces are presented. A study on contact angles for different functional groups grown on a silicon substrate is also provided.

Table of Contents

1. Contact Angle Measurements.....	2
2. How CA are measured	3
3. Temporal Evolution of CA in acid cleaned Silicon samples.....	5
4. Plasma Cleaning	8
5. Characterization of different functional groups on Silicon substrate	10

1. Contact Angle Measurements

The contact angle (CA) is the angle at which the liquid/gas interface meets the solid interface (See Figure 1).

Assuming that the solid surface is perfectly smooth it is easy to show that the system has to obey to the following equation, called Young equation:

$$\sigma_s = \gamma_{sl} + \sigma_l \cdot \cos \theta$$

Where σ_s is the surface tension of the solid phase, σ_l the surface tension of the liquid phase, γ_{sl} the interfacial tension between the two phases and θ the contact angle.

Measuring the contact angle θ and knowing the surface tension of the liquid and solid phases σ_s and σ_l it is possible to obtain the interfacial tension γ_{sl} and, through different methods, the surface energy of the solid.

A change in the surface structure (due to a re-arrangement of its molecules or to the interaction with the environment) can be hard to detect with a microscope, but it is easily detectable through a contact angle measurement. This because the structure change strongly influences the surface energy and consequently the contact angle.

It is in this case that contact angle measurements are used.

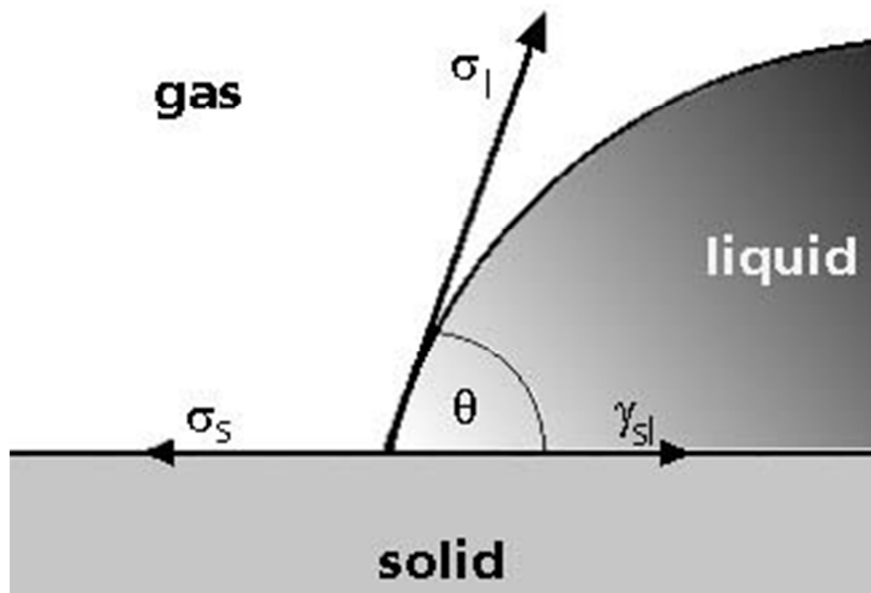


Figure 1 - The contact angle is the angle at which the liquid/gas interface meets the solid interface

2. How CA are measured

Contact angles are measured with “DataPhysics OCA35” contact angle machine and SCA20 software. The CA machine is composed by:

- A sample stage, where the specimen can be placed and its position precisely controlled.
- Three 0.5 mm diameter needles, connected to three different syringes, allowing dispensing a small amount of the desired liquid on the sample.
- An optical microscope, with the axis parallel to the sample stage surface, allowing to obtain an image of the droplet. This image is sent to the software, which perform the CA calculation.

A picture of the contact angle machine is shown in Figure 2.

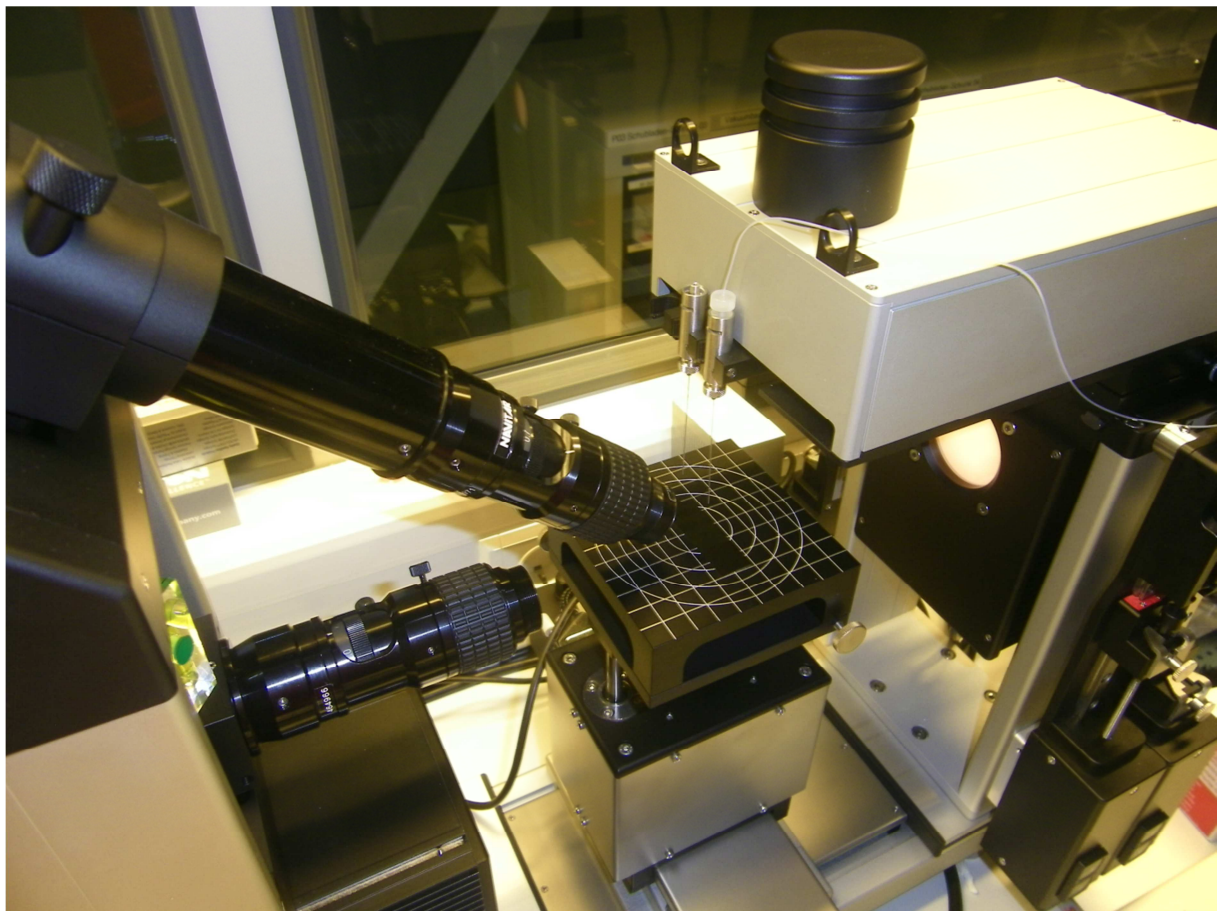


Figure 2 - The CA machine. On the left: the optical microscope. On the center: the sample stage with a silicon sample and the needles allowing to dispense drops on it. On the right: the syringes containing the liquids and a lamp allowing to obtain a better sample illumination.

To obtain a clear image of the droplet a few operations have to be performed:

- The sample stage has to be placed in a position allowing to see the specimen surface on the bottom part of the image.
- The focus of the optical microscope has to be adjusted in order to obtain a well-defined picture of the drop. To perform this operation without dispensing a droplet on the sample it is enough to place the needle near the sample (at a distance of a few millimeters) and focus the image on the needle. As it will be at the same distance from the microscope as the drop, the focus will be correctly set.

- The illumination has to be chosen with an intensity allowing to have a clear contrast between the drop and the sample surface. Generally intensities between 40 and 50 % are suitable for every type of measurement.

It is possible to operate on the machine with the manual commands just in front of it or through the software (**Device** -> **Device Control**, see Figure 3). Four types of operations can be done with the software device control:

- Illumination intensity control;
- Dispense units control: To choose the volume of the deposited drop and the speed at which it will be dispensed. It allows also to choose the parameters for an ARCA (Advancing and receding contact angle) measurement;
- EMD – Device: Used to define the position of the needle support;
- XYZ-Table: To define the sample stage position.

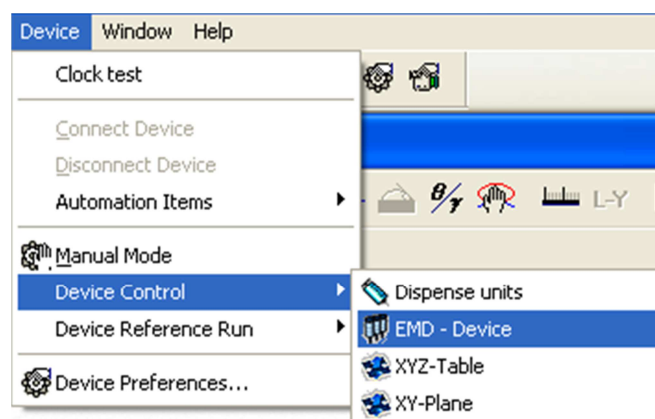


Figure 3 - The Device Control

Once all the preliminary operations have been performed, it is possible to dispense a drop and measure the contact angle. This is done through the Live Video window. It is necessary to choose the base line, to extract the drop profile and then to calculate the CA. The operation can be done automatically or in manual mode. A picture representing a measured CA is shown in Figure 4.

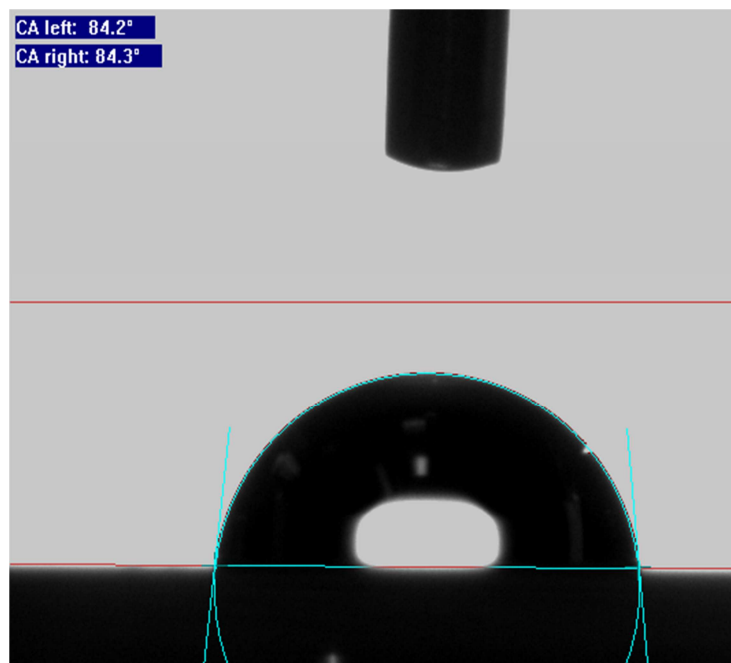


Figure 4 - A Measured Contact Angle

3. Temporal Evolution of CA in acid cleaned Silicon samples

A first analysis that has been performed with CA machine is the study of the CA evolution on acid cleaned Silicon samples with time.

The aim of this study is understanding for how much time the Silicon surface stays hydrophilic (it is after cleaning, but then interactions with air and dust change the surface behavior). This because the growth of a polymer layer is only possible when the substrate is hydrophilic.

To perform the analysis several acid cleaned samples have been prepared following the same procedure and a contact angle measurement has been performed on them at different times. This experiment has been done for samples conserved in controlled conditions (low pressure and humidity) and in room conditions.

The results are shown in the following tables and plots:

Controlled Conditions

Time ($\pm 0,5$ hours)	Contact Angle ($^{\circ}$)
1	0
3	0
24	0
44	$7,0 \pm 1,5$
50	$10,5 \pm 1,2$
68	$14,6 \pm 0,5$
140	$15,9 \pm 0,7$
191	$16,0 \pm 0,1$
309	$18,57 \pm 0,06$

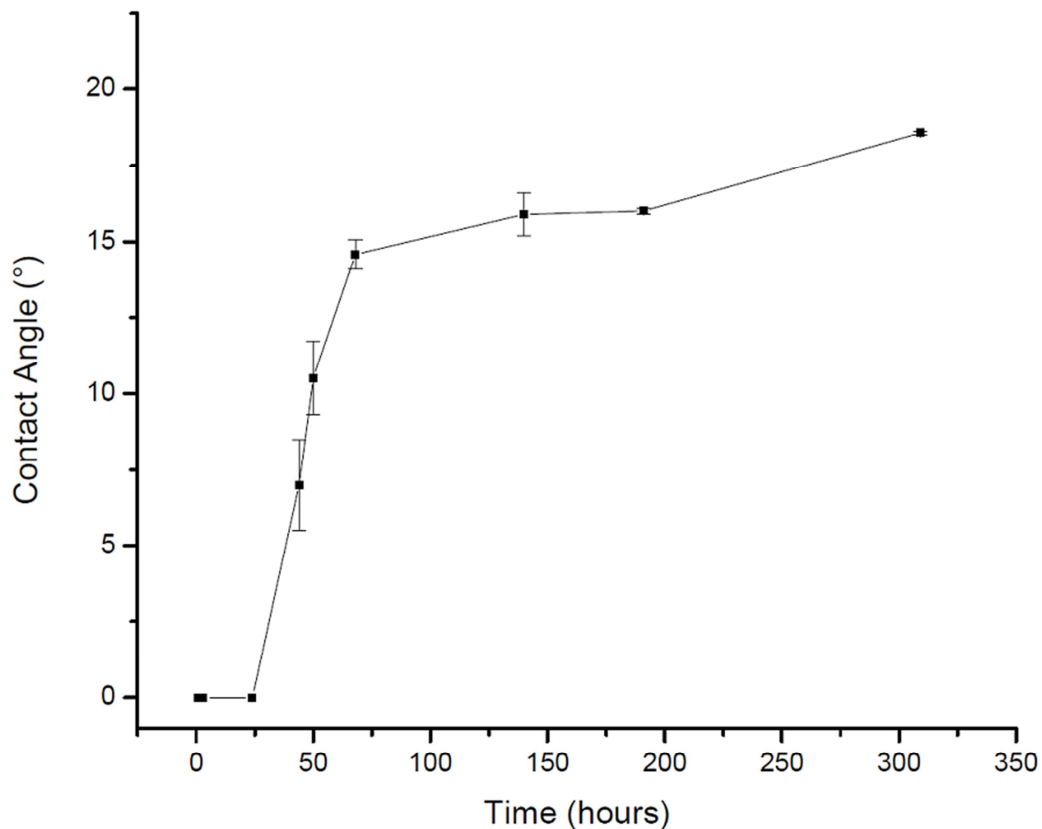


Figure 5 - Evolution of contact angles for acid cleaned silicon samples conserved in controlled conditions

Room Conditions

Time ($\pm 0,5$ hours)	Contact Angle ($^{\circ}$)
1	0
3	0
19	0
24	18 ± 2
44	15 ± 2
49	$9,1 \pm 0,5$
68	14 ± 1
139	$16,1 \pm 0,2$
190	$12,2 \pm 0,3$
318	$15,3 \pm 0,1$

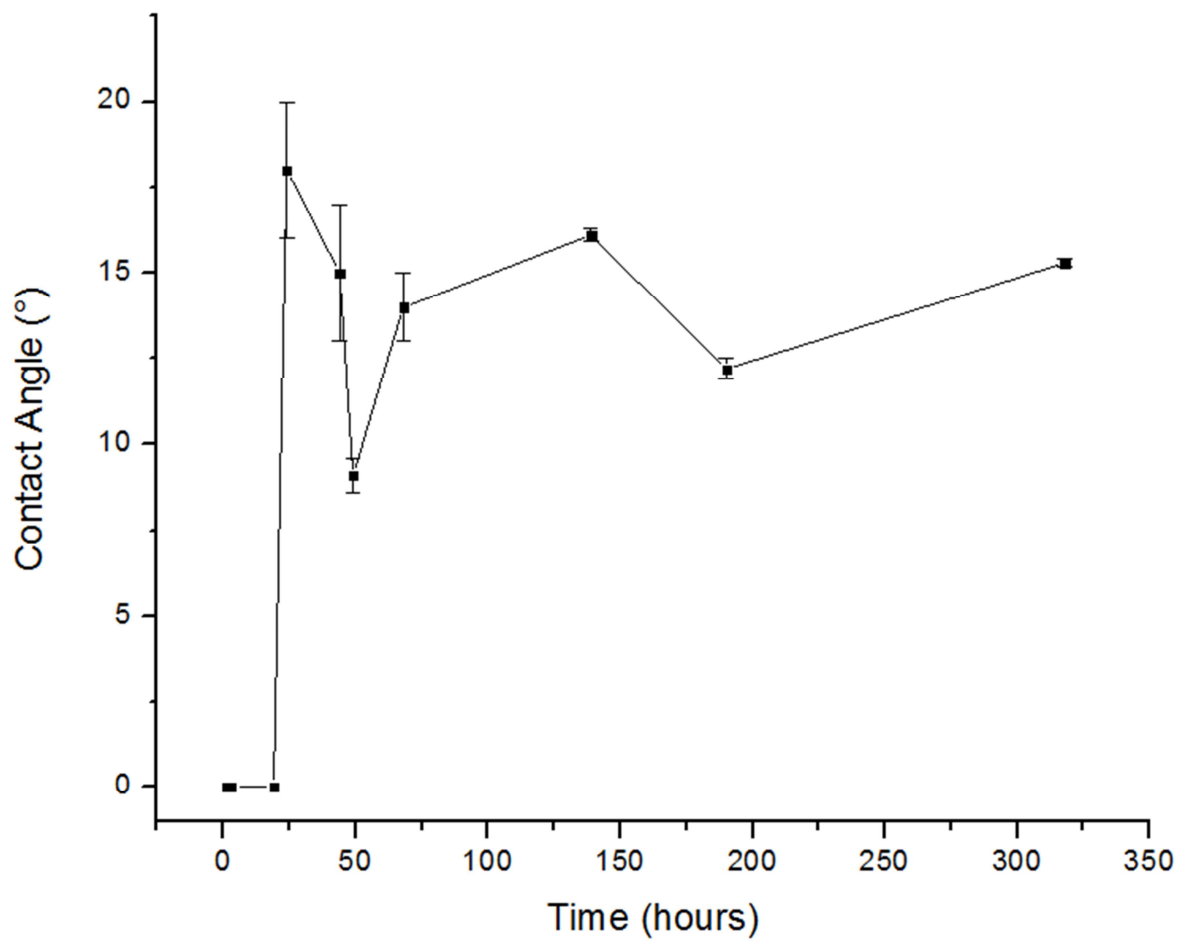


Figure 6- Evolution of contact angles for acid cleaned silicon samples conserved in room conditions

The error on the contact angle is reduced in the last measurements as they have been taken using an automation program, which allows repeating the measure always in the same conditions and in higher number.

In both cases we have perfect hydrophilicity until 24 hours from the cleaning and then a fast growth of contact angle in the following 20-40 hours (faster for samples conserved in room conditions than in controlled). After this quick step contact angles still increase, but with a lower slope.

Strong oscillations of CA can be noticed for samples in room conditions after the first step. This is probably due to less homogeneity, which causes bigger hydrophobicity in certain samples than in other.

Another series of measurements has been done on Silicon samples prepared with the same acid cleaning procedure (called GHBC samples), this time conserved only in room conditions.

The results are shown in the following table and plot:

GHBC Samples

Time ($\pm 0,5$ hours)	Contact Angle ($^{\circ}$)
9	$19,8 \pm 0,7$
35	$23,2 \pm 0,1$
57	$28,2 \pm 0,3$
121	$43,4 \pm 0,5$
177	$42,4 \pm 0,8$
201	$51,1 \pm 1,4$

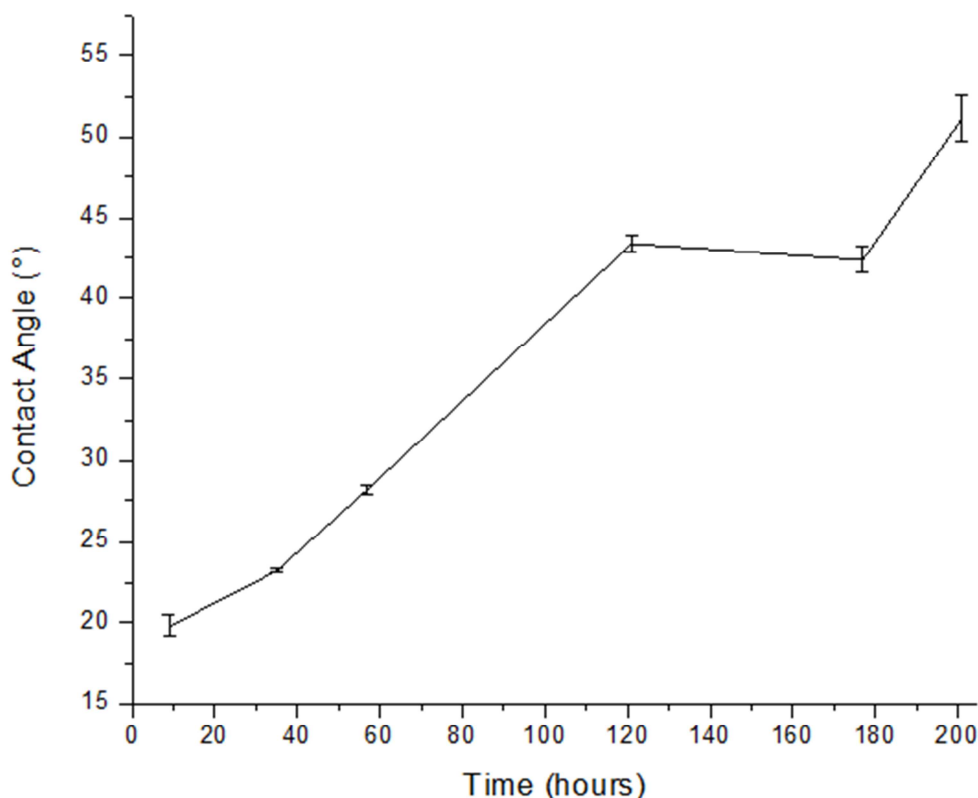


Figure 7 - Evolution of contact angle with time for GHBC samples

This time the contact angle reaches values near 20° after 9 hours from cleaning and they continue to rise with time, to values higher than 50° . No explanation can be provided to this fact without additional data.

4. Plasma Cleaning

An alternative technique to acid cleaning is the so-called plasma cleaning. The sample is placed in a vacuum chamber, where the pressure is set to a value of $10^{-2} - 10^{-3}$ mbar. When the machine is started oxygen atoms are ionized and interact with the sample, easily breaking the organic bonds. A picture of plasma cleaner is shown in Figure 8.



Figure 8 - Plasma cleaner

Plasma cleaning can be a suitable technique to tune the length of organic compounds grown on a Silicon surface. Regarding the exposure time of the sample with plasma, it is possible to reduce this length to the desired value. This value influences the contact angle of the surface (the more the chain is long, the more the contact angle is high). Consequently, plasma cleaning is a suitable way to tune the contact angle of an organic compound layer.

A preliminary study has been done and on a sample of octadecyl-trimethoxysilane (OTMS) grown on a Silicon substrate. The results show that:

- If the plasma production rate is not set to the lowest value all the organic compounds are scratched from the surface, even for very short times (≈ 5 seconds).
- If the plasma production rate is set to the lowest value, contact angles are reduced with a rate of:

$$6,7 \pm 0,4 \text{ } ^\circ/\text{s}$$

As it can be seen from the following plot:

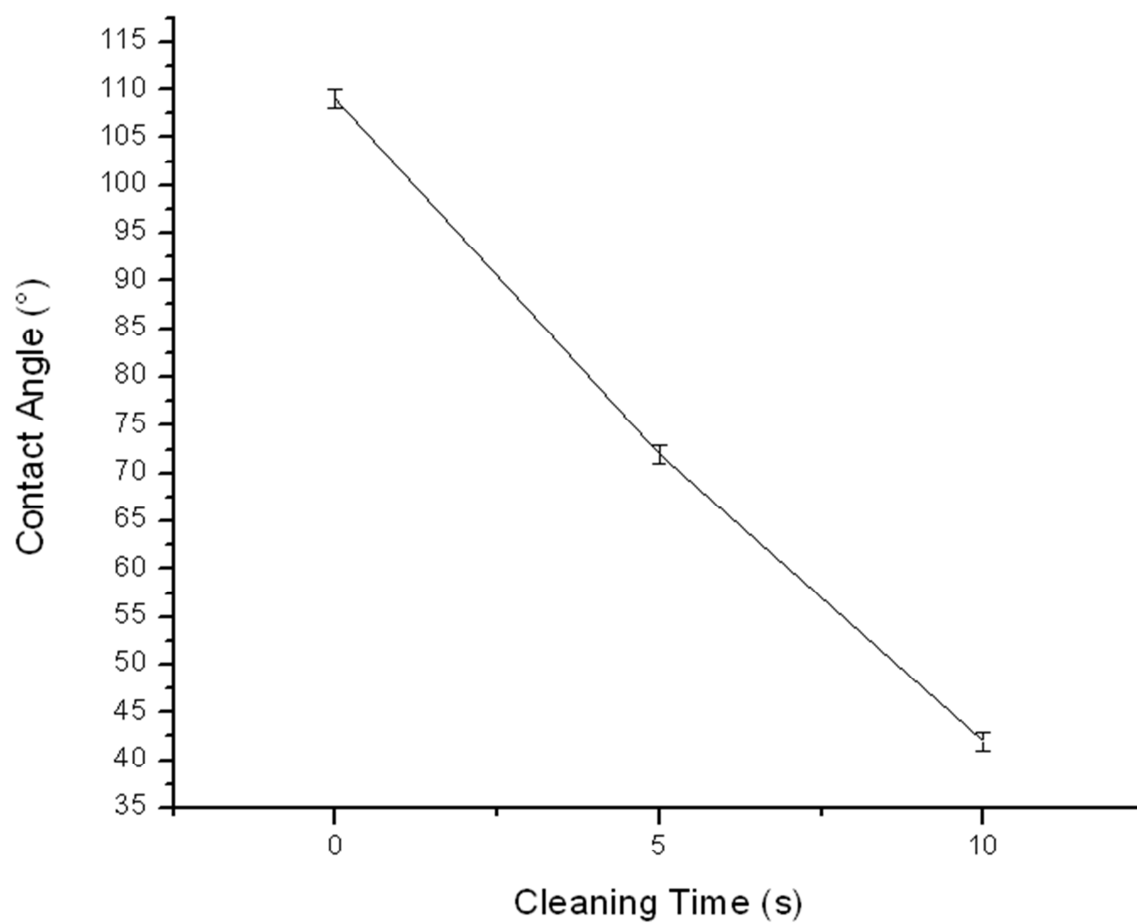


Figure 9 - Evolution of contact angles on a octamethylcyclotetrasiloxane layer after a certain cleaning time

Further studies can be done to obtain more experimental points on this curve and for other organic compounds.

5. Characterization of different functional groups on Silicon substrate

A last study that has been performed is the measurement of Contact Angles on different functional groups grown on a Silicon substrate. The purpose of these measurements is to have a resume of contact angles on different compounds in order to recognize them on unknown samples.

The measurements have been done within a few hours from the compound preparation.

The results of the measurements are shown in the following table and plot:

Compound	Contact Angle
EDTA	$42,2 \pm 1,7$
NH ₂	$70,0 \pm 0,5$
Ph	$75,2 \pm 0,5$
Sh	$64,2 \pm 0,4$

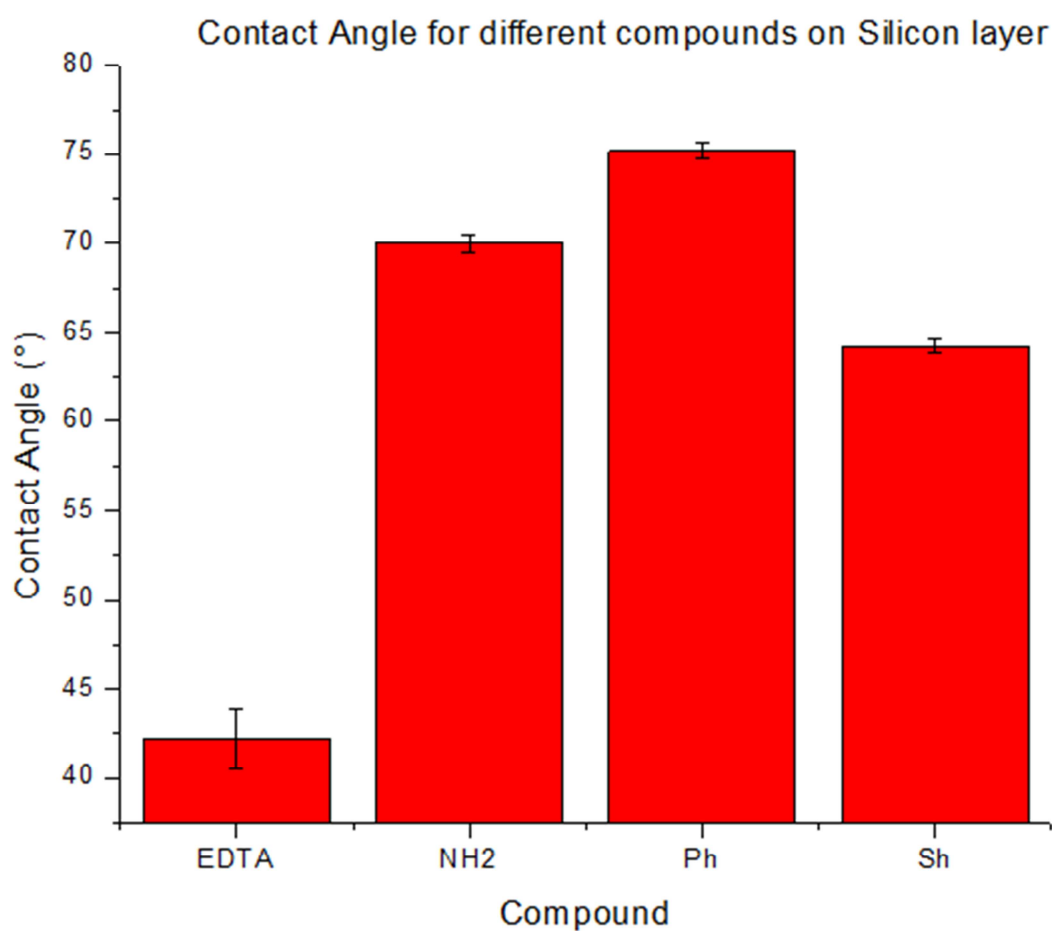


Figure 10 - Contact Angle for different compounds on Silicon layer