Composites in small and simple devices to increase mixing on detector surfaces

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Abstract. This work aims at three different applications for the betterment of plasma generated-composite thin films: pre-mixing, spray formation in miniaturized structures and an increase in the performance of detector surfaces. Miniaturized structures were projected, simulated with FEMLAB® 3.2 software and then constructed. Clustered films made from tetraethoxysilane (TEOS) and nonafluoro(iso)butyl ether (HFE®) precursors were deposited on silicon, acrylic and quartz substrates for different kinds of film characterization/or in the projected structures. Physical and chemical characterization guided the selection of best films previous to/after UVC exposure. The active surfaces (plasma-deposited films) in structures were modified by UVC exposure and then tested. The applications include pre-mixing of liquids and/or spray formation, best results being obtained with surface covered by derivative-HFE films, which acted as passivation layers. Preliminary results show good humidity sensing for TEOS-derivative films.

1. Introduction
TEOS (tetraethoxysilane) is the most common reagent used in the production of silicon oxide layers. The usual dry process includes plasma deposition, normally performed at high oxygen levels and high temperature. However, recently TEOS plasma polymerization at room temperature has come to the users attention, principally for flexible electronic structures and biosensors. In this case, low temperature is usually required to avoid degradation of the polymeric substrate [1]. In the absence of oxygen, TEOS polymerization leads to a hydrophobic silicone-like structure that can adsorb volatile organic compounds (VOCs) and water vapor. This polymeric chain can react when exposed to ultraviolet radiation, reactions presenting two main phases: initially carbon radicals are removed from the Si-O chain and SiOH is formed, generating a more hydrophilic surface. The second phase favors the appearance of Si-O-Si due to SiOH cross-link, restoring the hydrophobic character of the surface. If water is present, the film can suffer hydrolysis reaction forming a porous film with SiOH on the surface. Since acids or bases can catalyze this reaction, TEOS films present low resistance toward harsh environments [2]. As TEOS films are sensible to ultraviolet radiation (UV), alternating hydrophilic/hydrophobic surfaces can be created if some areas of the surface are exposed to UV. This

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prospect can be explored in the design of microstructures for micro-unit operations [3], as pre-columns in chromatographic micro-systems, micro-reactor systems or spray formation [4]. Three-dimensional micro-channels with different walls, i.e. half-sections of hydrophobic and hydrophilic surfaces, can separate immiscible phases [5]. Even planar structures, e.g. a sealed cavity, can allow mixing of water and 2-propanol [6] or water and glycerin, a viscous fluid [7]. Nonetheless, the mixing of water-oil samples is an important challenge for a micro-unit operation, because the fluids have different viscosities and low solubility’s. The low resistance of films to acidic and base solutions may hinder many of the possible applications, such as biosensors production.

Our previous work considered the tailoring of surface properties by co-deposition of HFE® (nonafluoro(iso)butyl ether) derivative plasma films: permeability to organic compounds, resistance to harsh environments or ultraviolet exposure, and oleophobic behavior was achieved by changing the film deposition parameters [8,9]. TEOS/HFE co-deposition leads to a good compromise between adsorption and resistance; preliminary results pointed out that miniaturized 3D-structures, with films on the inner surface modified by UV, might improve mixing of aqueous samples [10]. Our present work shows the use of composite thin films made from TEOS and HFE precursors in: 1) miniaturized structures for gas/liquid mixing or heterogeneous drop formation (spray); 2) passive layers on detector surfaces.

2. Experimental

Plasma composite thin films were produced using tetraethoxysilane (TEOS, Merck, USA, industrial grade) and/or methyl nonafluoro(iso)butyl ether (HFE®, 3M, USA, industrial grade). The DC powered plasma equipment was home-made and is described elsewhere. Three different substrates were used: 1) silicon wafers (type P, 100, 10-20 Ω·cm, Silicon Sense, Inc., USA), for composite characterization; 2) piezoelectric quartz crystal for water interaction tests (4.096 MHz, 8.0 mm diameter and 0.8 mm thickness, Hosonic Industrial do Brasil LTDA, Brazil); and 3) acrylics, for microstructures production and tests. All other reactants were P.A. grade and deionized water was used. The formed film was characterized after every step; every deposition step was followed by a concomitant deposition on silicon substrate. The following characterization techniques were carried out: a) ellipsometry to define refractive index, b) profilometry to determine the film thickness, c) optical and/or scanning electron microscopy (SEM) to observe cluster formation and/or roughness and d) contact angle measurements (using a goniometer and 4.0 μL drops of water) to evaluate capillarity (hydrophilic) characteristics. The corresponding SEM photos were analyzed with ImageJ® software in order to determine the distribution and the clusters size as deposited or after exposing to ultraviolet light (UVC, 1.8 W/m², 10 cm apart). Fourier Transformed Infrared Spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS) and Raman microscopy gave information about chemical characteristics of the films. Raman microscopy information was used to get insight about the chemical structure of the clusters. Resistance toward base/acidic aqueous solutions was evaluated by optical microscopy. QCM (quartz crystal measurements) experiments were performed with the piezoelectric crystals inside a controlled climate chamber.

The fluid behavior through microstructures, whose surfaces were pristine or exposed to UVC, was simulated using FEMLAB® 3.2b and two-dimensional or three-dimensional analysis, with an incompressible Navier-Stokes model. Differences in surface properties, such as hydrophobicity, were simulated according to Santos [11]. Santos considered two main trends: walls with and without interactions with the fluid. In the first case, the surface energy is different from zero; but no interaction means that the velocity is zero on the walls. The structures were projected and designed using Solid Edge ST4, Academic version, Siemens. They are: a) 3D-micro-channels: figure 1A presents the two parts that were machined from acrylic pieces using a conventional lathe in order to produce a single micro-channel. The surfaces of these parts can or cannot be modified by a plasma film/composite that was exposed to UVC. The micro-channel was 100 μm wide, 40 μm deep and 73 cm long, i.e. it has an area of 1.4 cm² and a volume of 1.1x10⁻³ cm³, being the area/volume ratio equal to 1,300. These structures were used for mixing or for spray formation purposes. For spray tests, the 3D-micro-channel
was coupled with a second structure, shown in figure 1B [4]. b) The micro-reactor: in this case, the inner part of structure (figure 1A) does not have the machined micro-channel (figure 1C) which increases the role of differences in the hydrophilicity of the surface. c) Sealed cavity: a planar device was manufactured and modified by plasma films and UVC exposure (figure 1D), as proposed previously with a different plasma film [7]. This device configuration maximizes the influence on hydrophilicity or oleophobicity.

Figure 1. Schematics of mechanical masks used to UVC exposure of (A) external and (B) internal parts of 3D structures and (C) planar structures.

The setups for insertion of nitrogen or air as gases [12] or water as liquid fluid [4] in the microstructures were described previously. The flow rate for gases was 5.0 sccm and ranged from 1.0 ml/min to 10.0 ml/min for liquids. Glycerin (650 cSt), mineral oil (viscosity of 43 cSt, Casa Americana, Brazil, tanned with Sudan black dye) or methylene blue aqueous solution (1% w/w) were used as tracers to observe fluid behaviour. Mechanical masks used for UVC exposures are represented in figure 2.

Figure 2. Schematics of mechanical masks used to UVC exposure of (A) external and (B) internal parts of 3D structures and (C) planar structures.

3. Results and discussion

This item presents the main characteristics of the plasma films and uses for the layers.

3.1. The film formation

The process of formation of plasma-composite films from TEOS or TEOS/HFE precursors and their main characteristics were described elsewhere [6,13]. The criteria for use considering the film characteristics are presented. The homemade plasma instrument made possible the production of clustered material. For films formed from TEOS and HFE, the main characteristics are:

1. Due to TEOS polymerization: a) graphite clusters can be formed and assure an adsorptive layer for VOCs; b) carbon radicals, such as OEt (etoxy), are present in the film, which
suggests the presence of silicone radicals. These radicals can react under UVC conditions, leading to SiOSi and/or SiOH formation, which leads to a more chemically resistant and less hydrophobic surface, respectively; c) water nucleophilic reactions can hydrolyze OEt radicals, leading to SiOH formation.

II. Due to HFE polymerization: a) some films present numerous organic clusters, formed mainly by fluorine organic compounds, which are hydrophobic, oleophobic and resistant to UVC exposure and acid and base solutions; b) films with few organic clusters presented low water contact angles but are still more resistant to acid/base solutions than TEOS samples; c) graphite clusters can be obtained in HFE films, but only for plasma at high power conditions, i.e., high ion bombardment on the surface.

Whereas TEOS/HFE composite samples are more useful as passive layers for mixing in miniaturized structures, TEOS films are suitable for sensor structures.

Table 1 summarizes the main characteristics of pristine films produced according to the selection criteria and the results after UVC exposure. Probably the oxidation during UVC exposure decreased cluster density and cluster size. Silicone clusters can be formed during exposure (ex.: samples A, B) due to a crosslink in TEOS-derivative films. Also SiOH can be formed, which contributes to lower water contact angles (ex.: samples A, C). The changing of the water contact angle is random; high values indicating hydrophobic surfaces. The surfaces were organophilic, and they were wetted by n-hexane and 2-propanol. The refractive index did not change significantly, ranging from 1.4 to 1.6, which is characteristic of samples with high carbon content.

Table 1. Main characteristics of TEOS and TEOS/HFE films, according to the selection criteria.

| Sample type | For TEOS film | | | For TEOS/HFE film | | |
|-------------|---------------|-----------------|-----------------|------------------|-----------------|-----------------|
|             | Before UVC    | After UVC       | Before UVC      | After UVC        | Before UVC       | After UVC       |
|             | Refractive index | Graphite clusters | Water contact angle | Silicone clusters | Water contact angle | Silicone clusters | Water contact angle |
|             |                | Size (µm²) / density (#/mm²) |                           |                    | Size (µm²) / density (#/mm²) |                           |                    |
| A           | 1.533          | 0.919 / 13,300   | 92               | 0.842 / 10,100    | 2.853 / 75        | 87               |
| B           | 1.522          | 0.326 / 22,800   | 99               | 0.198 / 21,000    | 0.308 / 37,300    | 98               |
| C           | 1.470          | 0.375 / 14,100   | 86               | 0.180 / 4,550     | 0.629 / 8,800     | 81               |
| D           | 1.488          | 0.394 / 22,200   | 101              | 0.150 / 6,600     | 0.292 / 197,000   | 95               |
| E           | 1.468          | 0.324 / 2,000    | 55               | 0.100 / 1,100     | nd               | 54               |
| F           | 1.429          | nd               | 29               | nd               | 0.125 / 54,000    | 33               |

Although deposition rates up to 20 nm/min can be achieved for these films, samples were produced at low range – 10 nm/min – because high rates require high plasma power and low precursor pressure. These plasma conditions promote high ion bombardment at the surface and, consequently, higher graphite concentration in the formed film. TEOS and TEOS/HFE films are composed of silicone-like structures with carboxyl and/or fluorine groups, respectively. Atomic concentration of oxygen is approximately 10% in all samples, as revealed by XPS, but it increases up to 17% after UVC exposure, which indicates that oxidation occurred on surface. The band for SiOSi in the FTIR spectrum was red-shifted by 20 cm⁻¹ after UVC exposure, revealing that polymer chains suffered cross-linking. FTIR bands for fluorine species at 1745 cm⁻¹ – 1640 cm⁻¹ region were weak. This
supports the results from XPS C1s deconvolution, that revealed a barely perceptible peak for fluorine species on the surface. CHn species were observed in the XPS spectra for pristine or UVC treated surfaces. Deconvolution of the C1s peak suggested the presence of graphite, whereas Raman microscopy revealed clusters formed by amorphous carbon (D band, 1300 cm\(^{-1}\) – 1500 cm\(^{-1}\)) and graphite (G band, 1600 cm\(^{-1}\)). The relative intensity of G and D bands was 0.5:1, respectively. These data differ from the corresponding information for samples obtained with plasma or photolytic procedures [14]. In summary, UVC exposure promotes several simultaneous reactions in the films, favoring crosslinks and/or oxidation of organic radicals and producing carbon clusters. Although the amount of fluorine is low, it was enough to protect the surface during 24 hours of UVC irradiation. All samples were acid and base tolerant, at least during 5 minutes of contact.

3.2. Uses

The main results obtained with the micro structures follow:

Figure 1 C shows the micro-reactor. The simulation of a water flow (5 ml/min) in such structures shows that the vorticity is homogeneous on all surfaces. The velocity of the fluid changes near the exit (Fig 3 A and B, respectively), i.e., a preferential path occurred. The creation of 4 hydrophobic zones changes this profile. Perturbations in the vorticity (Fig 3 C) and the velocity (Fig 3 D) occur in several points, and favor other paths. The corresponding experimental results (5 ml/min for water; 1 ml/min for mineral oil tanned with Sudan black) show: a) pristine films on the reactors surface favored one preferential path (Fig 4A); b) the UVC treated film, now with hydrophobic and hydrophilic (UVC treated area) zones, led to higher oil dispersion. The hydrophilic zone looked like an oil free area (Fig 4B).

![Streamlines for vorticity (A,C) and velocity (B,D) field in a micro-reactor.](image)

![Figure 3. Streamlines for vorticity (A,C) and velocity (B,D) field in a micro-reactor.](image)

![Figure 4. Water and mineral oil flows in structures (A) without and (B) with UVC exposure.](image)

These phenomena were enhanced in smaller dimensions; computer simulations predict the device performance. The fluid behavior on a 3D-micro-channel (Fig 1A) is similar to a chromatographic capillary column, with low vorticity and a velocity profile that does not change inside the channel [12]. On such conditions, a long and oleophobic channel full of water and oil (same conditions as figure 4) did not promote mixing. The oil fluid that travels through the channel dispersed and forms big drops with elongated shape inside the channel, as can be observed in the snapshots of figure 5A. When a micro channel with a surface modified by UVC irradiation was used, small drops (estimated volume 0.1 μL or less) were formed, and mixing is clearly observed (figure 5B). Simulations of velocity and vorticity profiles on such a micro-channel are shown in figure 5C. As the figure points out, differences...
in the surface hydrophilic/hydrophobic characteristics favored sudden variation in the velocity and the vorticity profiles. Similar behavior can be obtained for a gas flow (data not shown).

Figure 5. Experimental results: snapshots of oil interaction on a micro-channel (A) oleophobic; or (B) with hydrophilic/hydrophobic areas; (C) Simulation results: the velocity and the vorticity profiles on a micro-channel with hydrophilic/hydrophobic areas.

Two micro-unit operations [3] – mixing and spray formation – could be to advantage in using this system as a pre-mixing device. Figure 6A displays the difficulty of fluids with different viscosities, such as mineral oil and water, to be inserted simultaneously in the micro-channel that corresponds to the spray inlet system. In this experiment, the inlet capillaries were changed to ¼” plumbing, for illustration purposes. As can be seen in the figure, after 10 s of operation, some water was in the oil inlet, causing contamination and irreproducibility in the amount of oil admitted in the system. This occurred probably by an appreciable pressure dropping in the oil inlet system, since oil has high viscosity. On such condition (figure 6B), the spray interaction area will show a high volume of oil drops that were irregular showing different volumes, and they are not dispersed in the water. On the other hand, pre-mixing can decrease the pressure drop on the spray inlet system and the interaction area will show smaller oil drops. Moreover, the pre-mixing micro-channel could be used several times with mineral oil without interaction of oil and hydrophilic areas, since oil drops were not observed on that region. Figure 6C shows drops from a spray collected on a paper sheet positioned 10 cm from the outlet. As clearly pointed out by the color difference in the collected fluid, without UVC treatment of surface of the pre-mixing system, efficient mixing cannot occur and few oil drops will be observed in the exiting fluid. When some areas of the film were exposed to UVC, an apparent completed mixed sample was obtained.

Mixing can also be useful on a gas phase. A spike of VOC-contaminated gas phase was injected inside a micro-channel with pristine or a UVC treated surface. The VOCs composition was n-hexane:2-propanol mixtures in three distinct volume ratios: 1:9; 1:1; 9:1. Because the micro-channel is long, some separation can occur [2]. Two partially distinct Gaussian shapes are seen with a pristine surface on the channel. If the film on the surface of the micro-channel was treated with UVC radiation, a clear peak is not seen, in agreement with the interpretation that it is difficult to separate n-hexane/2propanol inside the channel. In other words, a mixing of n-hexane/2propanol inside the channel was promoted.

Pre-mixing is useful on detector surfaces because it decreases the limit layer, which allows more frequent interaction between the analyte and the sensing surface. Detectors usually are planar structures, similar to the sealed cavity presented in figure 1D. The performance of this cavity was simulated with changes in hydrophilicity; figure 7 shows the main results. On a cavity with a pristine surface, the vorticity was low with almost no changes. With a partial area in the bottom surface of the structure irradiated by UVC, the vorticity profile changed while the velocity streams remained almost equal. These results indicate that the overall fluid will pass through the structure easily, although some areas will induce interaction between fluid layers, i.e. favors mixing. The experimental results show good agreement with simulation. For a liquid phase composed of glycerin (0.1 ml/min or less) and water tanned with methylene blue (5.0 ml/min), the flow was disturbed in a device with a UVC treated surface, as can be seen in figure 8A. The mixing effect can be improved using the mechanical mask.
presented in figure 2C. As can be seen in figure 8B, the oil drops changed the original path several times because the oleophobic/hydrophilic surface (see detail in the figure 8B) favored mixing.

**Figure 6.** (A) Spray inlet system with water and mineral oil insertion. (B) Snapshots of oil interaction on a micro-channel with hydrophilic/hydrophobic areas after long use, and the spray interaction area whether pre-mixing is used or not; (C) drops formed with or without pre-mixing; (D) signal (a.u) at the outlet of a long channel UVC exposed or not.

**Figure 7.** Simulation of the vorticity (colors, s\(^{-1}\)) and the velocity (streamline) profiles using nitrogen (5.0sccm) in a sealed cavity (A) completely homogeneous or (B) half hydrophilic or (C) exposed with mechanical mask of figure 2C.
Figure 8. Experimental results for a sealed cavity: (A) blue-tinted water and glycerin sample retracts towards the hydrophilic half-surface of the cavity; (B) water and oil mixes in the cavity with an alternating UVC-treated/non-treated surface (the mask for UVC-treatment is presented in figure 2C); white and yellow lines enhance the hydrophobic and tinted water areas, respectively.

The films used in the previous shown experiments in the liquid phase had low sensitivity to VOCs, as quoted by QCM measurements. This is accomplished by choosing films with few carbon clusters. However, because these films are sensitive to water, they could play an important role in detecting water in the gas phase. Thus, the understanding of water-film interaction can address the design of miniaturized structures, as detectors, to improve their performance.

Figure 9 shows typical results for QCM measurements where humid air flows through a sealed cavity. In detecting humidity, TEOS films were more sensitive than TEOS/HFE films. UVC radiation degraded the sensitivity of films, whether made from TEOS or TEOS/HFE precursors, probably because fewer amounts of polymer were on the surface after the film treatment. However, UVC treatment improved water detection on TEOS films; relative humidity of 30% could be detected (Figure 9(A)).

Figure 9. Experimental results for QCM measurements of humidity on (A) TEOS or (B) TEOS/HFE films exposed or not to UVC.

4. Conclusions
This work shows advantages of using TEOS/HFE films treated under UVC radiation for the development of miniaturized structures. The performance of three different structures was tested: pre-mixing system, a micro-sprayer and a detector for humidity. All these achievements are based on changes of surface properties, the use of a feasible procedure and the predicting and understanding of phenomena with the help of simulations. An additional benefit is that the presented films and structures are environment-friendly.
5. References

[1] Coyle C, Gandiraman R P, Gubala V, Le N C H, O'Mahony C C, Doyle C, James B, Swift P, Daniels S and Williams D E 2011, Plasma Processes Polym. 9 1-28

[2] Carvalho R A M, Lima R R, Nascimento Filho A P, Silva M L P and Demarquette N R 2005 Sens. Actuators B 108 1-2, 955

[3] Yang Y Q 2008 Microscale and Nanoscale Process Systems Engineering: Challenge and Progress The Chinese Journal of Process Engineering 8 3 616

[4] Silva L M, Lima R R, Simões E W and da Silva M L P 2010 Int. Rev. Chem. Eng. 2 134

[5] Yamasaki Y, Kariyazaki A and Morooka S 2010, Int. J. Chem. Reactor Eng. 8 A 140

[6] Hernandez L F, Lima R R, Pecoraro E, Rosim-Fachini E and Silva M L P 2013 Mater. Sci. Forum 730-732 245, doi:10.4028/www.scientific.net/MSF.730-732.245

[7] Hernandez L F, Jesus A A, Lima R R, Fachini E R, and Silva M L P 2012 Small and Simple Devices for Increase Mixing on Detector Surfaces 14th Int. Meeting Chem. Sensors (Nuremberg) - IMCS 2012 May 20-23 AMA Science Portal doi:10.5162/IMCS2012/P2.9.2

[8] Lima R R, Hernandez L F, Pecoraro E, Rosim-Fachini E and Silva M L P 2013 Mater. Sci. Forum 730-732 232 doi:10.4028/www.scientific.net/MSF.730-732.232

[9] Lima R R, Hernandez L F, Pecoraro E, Rosim-Fachini E and Silva M L P 2013 Mater. Sci. Forum 730-732 289 doi: 10.4028/www.scientific.net/MSF.730-732.289

[10] Hernandez L F, Leite A R, Lima R R, Fachini E R, and Silva M L P 2012 Adsorbent Composites Used on Mixing in Miniaturized Structures 14th Int. Meeting Chem. Sens. (Nuremberg) – IMCS 2012 May 20-23 AMA Science Portal doi:10.5162/IMCS2012/P2.8.3

[11] Santos L C, Beraldo F P, Simões E W, Carvalho A T and Silva M L P 2008, Sens. Actuators B 130 310

[12] Carvalho A T, Lima R R, Silva L M, Simões E W and Silva M L P 2009 Sens. Actuators B 137 393

[13] Hernandez L F, Lima R R, Pecoraro E, Rosim-Fachini E and Silva M L P 2013 Mater. Sci. Forum 730-732 185 doi:10.4028/www.scientific.net/MSF.730-732.185

[14] Dartois E, Muñoz-Caro G M, Deboffle D, Montagnac G and d'Hendecourt L 2005 A&A 432 895 doi:10.1051/0004-6361:20042094