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How the chemical structure of the plasma-deposited SiO_x film modifies its stability and barrier properties: FTIR study

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Abstract

Organosilicon thin films issued from the gas mixture of oxygen and hexamethyldisiloxane (HMDSO), 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS), or fluorotriethoxysilane (FTEOS) deposited on polycarbonate (PC) substrate were obtained thanks to a RF plasma source. The chemical structure of the two types of inorganic SiO_x (HMDSO/O₂, TMCTS/O₂) and fluorinated SiO_xC_yF_z (FTEOS/O₂, FTEOS/O₂/TMCTS) coatings have been investigated by FTIR and XPS spectroscopies, and wettability measurement. Network structure and density of SiO_x and SiO_xC_yF_z thin films were discussed as a function of the νSiOSi band shifting observed in their respective FTIR spectra. The influence of various plasma parameters (such as discharge power, precursor/O₂ ratio and, duration) on the film properties was studied in order to optimize the growth of both inorganic and fluorinated thin films. The ageing of such layers either at ambient atmosphere or even at reduced pressure showed a chemical alteration

of the thin films surface and bulk, which stabilized after 15 days of storage. Such phenomenon is explained by the hydrophobicity recovery that may induce the observed network alteration. Water and oxygen permeation and transport properties of treated PC films were correlated with the coating structure and composition; then TMCTS was identified as the most efficient precursor for enhancing water barrier property. Furthermore, the permeation properties of these deposits seem to be more controlled by the material density than by their chemistry

Key-words: inorganic silicon; fluorinated silicon; PECVD; density; permeation.

I. Introduction

Over the last few years, there are a lot of developments in the area of new barrier coating technologies. The innovations were developed in three major axes: (a) thin coatings; (b) new barrier polymers, (c) nanocomposite materials [1,2]. Among these, the deposition of organosilicon thin film onto plastic substrates attracted more and more attention because of the high barrier property towards the oxygen gas (or other permeant molecules) but also due to the optical property of the synthesized layer [3,4]. The barrier thin film can be produced either by physical vapor deposition (PVD) [5,6], namely by the sputtering or the evaporation of a solid precursor assisted by an electron beam, or by plasma enhanced chemical vapor deposition (PECVD) of gaseous organosilane and oxygen mixture [4,7,8].

The literature reported that inorganic SiO_x layer deposited by PECVD is considered as one of the best barrier coatings thanks to its dense structure. Different natures of transparent (inorganic SiO_x and organic $\text{SiO}_x\text{C}_y\text{H}_z$) deposits from different precursors (silane or siloxane compounds) is investigated [3,4,7,8]. The improvement in barrier properties depends mainly on the deposition process, i.e. the plasma parameters for the plasma technology. A. Grüniger *et al* [3] demonstrated that the HMDSO/ O_2 RF (Radio Frequency) plasma is more efficient than MW (Microwave) source in terms of the oxygen transmission rate (OTR) which respectively

varied from 0.61 to 11.7 cm³ (STP) m⁻² day⁻¹. Such oxygen resistance was related to the density which is higher for RF (2.03 g.cm⁻³) compared to MW (1.80 g.cm⁻³) [3]. The OTR value is also decreased with the increase of RF power and oxygen addition. Indeed, a high proportion of oxygen in HMDSO/O₂ mixture, from 1/3 to 1/18, is needed for increasing the density [3,9] since the oxygen atoms in the plasma phase ablate the carbon moieties and therefore reduce the carbon/silicon ratio in the film from 0.47 to 0.26 [9]. However, the diffusion through the thin film seems to be governed by pinholes defects. These pinholes were related to the presence of carbon and hydrogen atoms in the bulk structure [10,11]. Indeed, pure inorganic SiO_x coating showed a gas barrier effect higher than that observed for the corresponding organic SiO_xC_yH_z film. Similarly, Charifou *et al.* [7] showed that the OTR values of thin films prepared from trimethylsilane (TMS) and hexamethyldisiloxane (HMDSO) precursors were lower for the inorganic coating (0.07 and 0.2 cm³ (STP) m⁻² day⁻¹ for TMS and HMDSO, respectively) compared to its equivalent organic film (0.94 and 1.11 cm³ (STP) m⁻² day⁻¹ for TMS and HMDSO, respectively). Same conclusion can be drawn in function of the oxygen partial pressure.

In addition to the influence of the inorganic character of the barrier layer, the fluorination of the polymer surface can improve the barrier property of the plastic substrate. Indeed, the influence of hydrophobic plasma-treatment (CF₄, CF₄/ H₂, CF₄/ C₂H₂, or SF₆) on the polylactic acid (PLA) or on the poly(ethylene-*co*-vinyl alcohol) (EVOH) films surface were investigated for such a purpose [12-13]. The simple fluorine atom grafting induces the increase of the hydrophobicity of plastic film surface that leads to the decrease of its water permeability. N. Tenn *et al* found that the hydrophobicity was significantly improved after plasma treatment and the water permeability of some of these PLA plasma-treated films was decreased down to 28 % [13]. Furthermore, the *ab initio* molecular orbital method described an improving water resistance of SiOF film [14]. Consequently, carbon and fluorine-doped silicon oxide (SiO₂:C,F)

films have been deposited from mixture of tetraethoxysilane (TEOS), C₄F₈ and Ar by plasma enhanced chemical vapor deposition (PECVD) [15]. Such a study showed that the film containing more SiF bonds than SiF₂ ones had excellent resistance to water and thermal stability. As an example, plasmas rich in fluorine atoms, by adding CF₄ to SiH₄/N₂O, led to the formation of Si-F bond rather than to Si-F₂ one and also caused the Si-OH appearance. As a consequence, the prepared films presented lower water absorption [16].

The aim of this work is to study the influence of the two types of silicon-derived thin films, i.e. inorganic SiO_x and fluorinated silicon SiO_xC_yF_z as function of their density and hydrophobic character. The density characterized by the Si-O-Si conformation will be determined by varying the plasma parameters for different precursors. Two precursors were selected: the linear hexamethyldisiloxane (HMDSO) and the cyclic 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS), the latter having a lower carbon proportion. The hydrophobic character of SiO_xC_yF_z layer will be modulated by the homopolymerization of fluorotriethoxysilane (FTEOS) or its copolymerization with TMCTS. Their resulting water and oxygen transport properties will be described. Furthermore, the discussion will be also focused on the long-term stability of such layers and how the ageing performed in different atmospheres could modify either the network structure or the hydrophobicity behavior.

II. Experimental part

II.1. Elaboration of SiO_x and SiO_xC_yF_z thin layers

Hexamethyldisiloxane (HMDSO, (CH₃)₃SiOSi(CH₃)₃, Sigma Aldrich, ≥ 98% purity), 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS, (HSiCH₃O)₄, Sigma Aldrich France, ≥ 99.5 % purity), fluorotriethoxysilane (FTEOS, (CH₃CH₂O)₃SiF, Alfa Aesar, ≥ 95 % purity), O₂ (99.99 % purity, Air Liquid), Ar (99.99% purity, Air Liquid) were used as received. Coatings were

directly deposited on polycarbonate (PC) substrates for wettability measurement, on Si/SiO₂ wafer for XPS spectroscopy and on pressed KBr pellets for FTIR spectroscopy.

Plasma was excited with a radio-frequency (RF-power 13.56 MHz) capacitive coupling plasma reactor (MG300S, Plassys) consisting in a cylindrical aluminum chamber (28 cm in diameter and 6.15 L volume) with two parallel circular electrodes (20 cm in diameter) which are separated by 9.5 cm. The substrates were positioned on the cathode (lower electrode) during the film formation process. In order to ensure good adhesion of the deposit, the polymer substrate surface was pre-activated by Ar plasma (flow: $F_{Ar} = 10$ sccm, discharge power $P = 100$ W, total pressure $p = 0.02$ Torr, duration $t = 30$ s). Then, the evaporated precursor (HMDSO, TMCTS, FTEOS) and oxygen were simultaneously but independently injected at the top of the chamber thanks to an electrode-integrated shower. Chamber pressure was detected by a gauge. Precursor gas was injected with controlled pressure, then O₂ gas was added at a desired ratio. The oxygen partial pressure was calculated as the difference between total pressure and precursor pressure. In case of copolymer FTEOS/O₂/TMCTS, TMCTS gas was injected after FTEOS gas introduction and before O₂ addition. Thus, partial pressure of each gas was determined as the difference of total pressure before and after its introduction in mixture. The chamber pressure was maintained constant at 0.02 Torr during the plasma polymerization process. The following plasma parameters were varied: pressure ratio of precursor to O₂ r (from 1:1 to 1:7.5), discharge power P (from 50 to 150 W), deposition time t (from 1 to 5 min).

Organosilicon films deposited onto KBr pellets and PC substrates were storage under two different conditions at room atmosphere and at reduced pressure at 740 mm of Hg (0.09MPa) during 30 days. Chemical and wettability evolution of thin film was followed by FTIR spectroscopy and water contact angle (WCA) measurement.

II.2. Film characterization

FTIR spectroscopy

Information about structure and compositional properties of the SiO_x and SiO_xC_yF_z films onto transparent KBr pellets was obtained from Bruker Vertex 70v spectrometer with 2 cm⁻¹ resolution in the range 4000 - 400 cm⁻¹, 20 scans were averaged. The FTIR measurements were done approximately 10 min after removing the sample from the reactor. Spectra were treated with Opus software for baseline correction and CO₂/H₂O subtraction. All the spectra were normalized by the thickness of the thin film.

Water contact angle and adhesion measurements

Wettability of the thin films on PC substrate was carried out by using a goniometer with 3μL of high purity water drops (MilliQ Water System, resistivity 18MΩ cm⁻¹). Measurements were made on both sides of 5 drops and then averaged. Each result is the average of five experiments, i.e. average of 10 different values. The PC roughness estimated around 100 nm should not interfere with the measure since a 3μL drop was deposited.

The adhesion of the SiO_x and SiO_xC_yF_z thin layers on PC substrate was measured by the scotch tape normalized test (ASTM D3359 – 17). It appears that all the synthesized films are adherent. No delamination of the plasma-deposited layer and no weak boundary layer that may alter the contact angle measurements are observed.

X-Ray Photoelectron Spectroscopy (XPS)

The different films plasma-deposited onto Si/SiO₂ wafers were analyzed by XPS (Kratos Axis Nova, UK) at the Institut des Matériaux de Nantes, France. The photoemission was excited by a monochromatic Al Kα beam. The spectra were recorded with the electron emission angle at 90° to the sample surface. All binding energies (BEs) were referenced to the C_{1s} hydrocarbon peak of C-C at 285 eV. In curve fitting, the line width (full width at half-maximum, FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. The elemental quantification accuracy was 5%.

Atomic force microscopy (AFM)

The thickness of the deposited organosilicon film was determined on Si/SiO₂ wafer by AFM (Bruker Innova). A mask was placed on a part of the substrate before the deposition. Once the deposition was finished, the mask was removed and the top level corresponded to the thickness of the organosilicon film was measured. Areas of 50 x 50 μm² of the coated Si/SiO₂ substrate were scanned in tapping mode at ambient air. The film thickness was determined using Gwyddion software.

Water permeation measurements

Water permeation kinetics through the PC film before and after deposition of SiO_x and SiO_xC_yF_z were measured at 25°C using the home-made permeadiffusimeter [17]. After a drying step with a dry nitrogen, the upstream compartment of the permeation cell containing the film was filled with the liquid water (MilliQ water system, resistivity 18 MΩ cm⁻¹). The water transfer through the PC film was measured as a function of time by controlling the variation of the dew-point temperature. The permeability coefficient P (expressed in Barrer unit: 10⁻¹⁰ cm³(STP).cm.cm⁻².s⁻¹.cmHg⁻¹) was then determined from the product of the stationary flux by the film thickness and divided by the difference in water activity on both sides of the film (liquid water in upper side and nitrogen gas in downside, so $\Delta a=1$).

Oxygen permeation measurements

The measurements were carried out using a home-made apparatus. PC film was placed between the upstream and the downstream part of the permeation cell and dried for 17 h under vacuum. Then, the oxygen gas was introduced into the cell upstream compartment at a constant pressure of 4 bars until the steady state was reached. The permeability of the film to oxygen P determined the gas quantity passing through the film was calculated by “time-lag” method.

III. RESULTS AND DISCUSSION

III.1. Chemical structure of SiO_x and SiO_xC_yF_z (co)polymers

The influence of the plasma parameters was studied in order to obtain a low carbon and hydrogen content and to preserve the fluorine concentration in the case of SiO_xC_yF_z layer. The chemical structure of deposited films (HMDSO/O₂, TMCTS/O₂, FTEOS/O₂, FTEOS/O₂/TMCTS) at fixed plasma parameters ($P = 100$ W, $t = 2$ min) with $r = 1/5, 1/5, 1/1, 4/4/1$ respectively for HMDSO/O₂, TMCTS/O₂, FTEOS/O₂, FTEOS/O₂/TMCTS is analyzed by FTIR spectroscopy (Fig. 1). In Table 1, all vibration bands are assigned. Spectra (Fig. 1, left) and Table 1 show three vibration modes of Si-O-Si bond at about 1060, 800 and 460 cm⁻¹ corresponding respectively to the stretching, bending, and rocking vibration modes. The Si-OH (stretch), Si-H (stretch), C=C (stretch), CH₃ (bend) vibrations are also identified on SiO_xC_yF_z type spectra thanks to the vibration peaks at around 3500 - 3750, 2250, 1623 - 1619, 1383 cm⁻¹ band, respectively. Apparently, the hydrocarbon proportion associated to the intensity of 2925 and 1383 cm⁻¹ FTIR bands in the fluorinated copolymer seems to be lower compared to that for FTEOS/O₂ deposited layer. The main effect of the fluorine incorporation is the appearance of the vibration band ranging from about 900 to 1000 cm⁻¹ on FTEOS/O₂ and FTEOS/O₂/TMCTS spectra; assigned to the contribution of stretching vibration of Si-F_x groups. Some C-F absorptions could also contribute to the Si-O-Si absorption band. However the results of XPS analysis of FTEOS/O₂ and FTEOS/O₂/TMCTS layers, discussed later, indicates smaller F/C ratio (0.05 - 0.08) than that of O/C (1.01 - 1.78) and the high resolution C_{1s} peak (not shown here) of both layers do not reveal any presence of C-F bond.

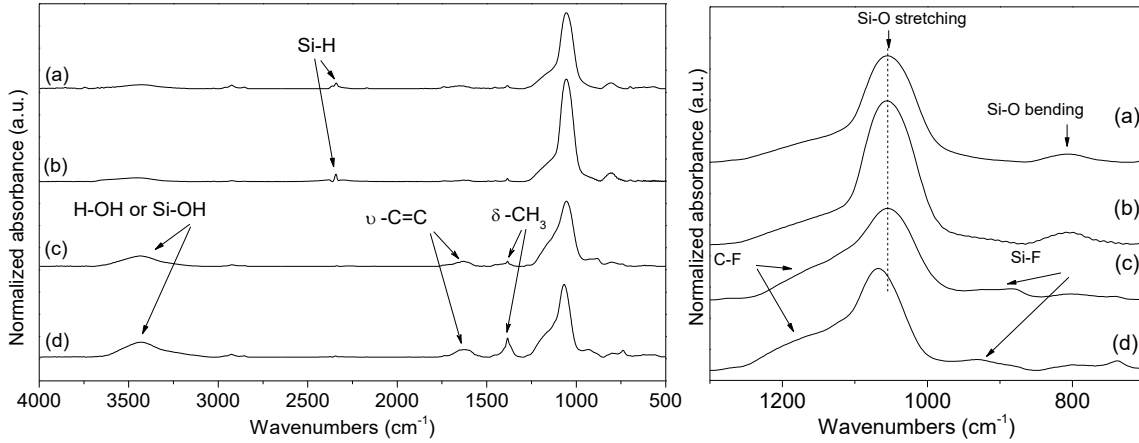


Fig. 1 FTIR spectra (left) and its zoom between 1300 - 700 cm^{-1} (right) of films deposited from (a) HMDSO/ O_2 (1/5), (b) TMCTS/ O_2 (1/5), (c) FTEOS / O_2 / TMCTS (1/4/4) and (d) FTEOS/ O_2 (1/1) ($P = 100 \text{ W}$, $p = 0.02 \text{ Torr}$, $t = 2 \text{ min}$)

Table 1 FTIR band assignment of SiO_x and $\text{SiO}_x\text{C}_y\text{F}_z$ plasma films ($P = 100 \text{ W}$, $p = 0.02 \text{ Torr}$, $t = 2 \text{ min}$)

Assignment	IR absorption (cm^{-1})			
	HMDSO/ O_2	TMCTS/ O_2	FTEOS/ O_2 /TMCTS	FTEOS/ O_2
OH stretch	3440 (w)	3440 (w)	3440 (s)	3440 (s)
CH_3 stretch	2925 (w)	2925 (w)	2925 (w)	2925 (w)
SiH stretch	2343 (w)	2343 (w)	-	-
C=C stretch	1623 (w)	1619 (w)	1623 (s)	1623 (s)
CH_3 bend	1383 (w)	1383 (w)	1383 (w)	1383 (s)
SiOSi stretch	1055 (vs)	1055 (vs)	1055 (vs)	1068 (vs)
SiF stretch	-	-	922 (w)	922 (w)
SiOSi bend	800 (w)	800 (w)	800 (w)	800 (w)
SiC bend	-	-	740 (w)	740 (w)

w: weak intensity, s; strong intensity, vs: very strong intensity

This detailed FTIR study highlights two features: the shift of νSiO wavenumber maximum to higher or lower wavenumbers compared to the peak position of purely SiO_2 structure (1060 cm^{-1}) [4,18] and the broadening of this main band. As stated above, the fluorine

and carbon attachment in FTEOS/O₂ deposit shifts the Si-O-Si band position to higher wavenumber (1068 cm⁻¹) while the Si-O-Si stretching band is centered at 1055 cm⁻¹ (lower value) for TMCTS/O₂ and HMDSO/O₂, FTEOS /O₂/TMCTS (Fig. 1, right). Such a Si-O stretching frequency shift is related to the alteration of the bonding properties of inorganic structure, such as the bond angle and the bond length [4,19,20]. The predictive model [21] based on the local atomic structure, in particular the bond angle 2θ, at the intertetrahedral bridging oxygen atom sites, showed that the average or central frequency of the Si-O-Si stretching vibration is expressed as:

$$\nu = \nu_0 \sin\theta, \text{ (Eq. 1)}$$

where $\nu_0 = 1116.5 \text{ cm}^{-1}$ (experimentally obtained for $\theta = 75^\circ$ in thermal silica films) [21]. From Eq. (1), as ν increases, θ also increases and indicates that the network structure is more relaxed probably due to the formation of large ring structures. Furthermore, Y. Kim *et al* [22] introduced the “bonding structure model” based on the atomic “electro-negativity”. The fluorine attachment will lead to a different polarization and will distort the Si-O-Si bond and will induce the shift of Si-O-Si stretching band to a higher wavenumber [23,24]. The opposite effect is observed with the presence of carbon or hydrogen atoms (such as Si-H bond which vibration mode is centered at 2343 cm⁻¹) because of their lower electron-negativity than oxygen and fluorine ones and also of the appearance of smaller rings [4,22,25].

The second feature is associated to the Si-O-Si band broadening which is bigger for the fluorinated layers. According to P.G. Pai *et al* [26], this fact is related to a statistical distribution of different bonding arrangements at each silicon atom site induced by the presence of carbon and fluorine atoms and leading to the formation of defects in the SiO_x network. Higher the proportion of F or C and O atoms is, broader the Si-O-Si band is. So, these layers should be considered to be organic rather than inorganic and dense.

The chemical structure of the surface of the four deposits was studied by XPS analysis. The elemental composition obtained from the broad XPS spectra is given in Table 2. For the studied plasma parameters, the deposited layers have this following stoichiometry: $\text{SiO}_{1.5}\text{C}_{0.1}$ for TMCTS/ O_2 , $\text{SiO}_{1.3}\text{C}_{0.1}$ for HMDSO/ O_2 , $\text{SiO}_{1.4}\text{C}_{0.8}\text{F}_{0.1}$ for FTEOS/ O_2 /TMCTS and $\text{SiO}_{1.5}\text{C}_{1.4}\text{F}_{0.1}$ for FTEOS/ O_2 . Higher carbon concentration is found in the case of fluorinated $\text{SiO}_x\text{C}_y\text{F}_z$ layer compared to SiO_x type, lower than 5 %, i.e. around 24.3 % for the fluorinated homopolymer and 36.5 % for the copolymer. Such a behavior for all cases could be explained by an insufficient proportion of oxygen in the plasma phase to remove the carbon part. Indeed, pure silica (SiO_2) would provide an O/Si ratio of 2 while the ratio of two inorganic and unfluorinated SiO_x layers is lower around 1.3 - 1.5. These results confirm the presence of CH_3 and Si-H vibration bands observed on FTIR spectra (Fig. 1 and Table 1). In case of fluorinated $\text{SiO}_x\text{C}_y\text{F}_z$ type, the plasma copolymerization of TMCTS and FTEOS reduces carbon content (36.5% for the homopolymer and 24.3% for the copolymer) and therefore enhances the silica proportion compared to the plasma homopolymerization of FTEOS. The thin film issued from the cyclic monomer was found to have the most inorganic structure thanks to a higher O/Si and a lower C/Si ratio. This result may be explained by the elemental composition of both precursors, the cyclic one bearing less carbon atoms and more oxygen ones. Lastly, since the film density is related to the stoichiometry [27], the lower C/Si ratio states an increasing dense network compared with the silicon oxide films: $\text{FTEOS}/\text{O}_2 < \text{FTEOS}/\text{O}_2/\text{TMCTS} < \text{HMDSO}/\text{O}_2 < \text{TMCTS}/\text{O}_2$.

Table 2 Atomic concentration and ratio of films deposited from HMDSO/ O_2 (1/5), TMCTS/ O_2 (1/5), FTEOS/ O_2 /TMCTS (1/4/4) and FTEOS/ O_2 (1/1) ($P = 100 \text{ W}$, $p = 0.02 \text{ Torr}$, $t = 2 \text{ min}$)

	Atomic concentration (%)				C/Si	O/Si	F/Si
	C_{1s}	O_{2s}	Si_{1s}	F_{1s}			
HMDSO/ O_2	4.5 ± 0.2	54.3 ± 2.7	41.3 ± 2.1	–	0.1	1.3	–
TMCTS/ O_2	3.4 ± 0.2	57.8 ± 2.9	38.9 ± 1.9	–	0.1	1.5	–
FTEOS/ O_2 /TMCTS	24.3 ± 1.2	42.8 ± 1.7	30.8 ± 1.5	2.0 ± 0.1	0.8	1.4	0.1

FTEOS/O ₂	36.5 ± 1.8	36.9 ± 1.8	24.9 ± 1.2	1.7 ± 0.1	1.5	1.5	0.1
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To obtain a better insight into the chemical bonds of the organosilicon surfaces, high resolution O_{1s} and Si_{2p} spectra were performed and results are reported in Table 3. The decomposed O_{1s} peak presents two substructures with the bond energies at respectively 532.2-532.7 eV and 533.2 - 533.9 eV. The highest band energy is assigned to SiO₄ structure as reported in [28-30]. It also appears that all of the four layers contain a quite similar content (80 - 90 %) of X-SiO₃ bond (X = CH_nF_m in fluorinated type or H in non-fluorinated type), which is greater than the proportion of SiO₄ bond (10 - 20 %). In case of silicon oxide type, higher SiO₄ content in TMCTS/O₂ thin film suggests a more inorganic structure than HMDSO/O₂ one. On the other hand, even if the SiO_xC_yF_z thin film bears carbon and fluorine pendant groups, such layer presents high SiO₄ proportion, higher than in the case of HMDSO deposited layer.

The high resolution Si_{2p} peak allows discriminating the different substitutions of Si atom: Si(-O)₁, Si(-O)₂, Si(-O)₃, Si(-O)₄ with an increased bond energy in respect to the oxidation level [31]. Therefore, substructures at low binding energy values 101.1 - 101.7 eV were assigned to X₃-SiO, X₂-SiO₂. These structures are formed only during the homo and copolymerization of fluorinated precursors while the other substructures attributed to X-SiO₃ and SiO₄ are detected in all cases. The -SiF group also contributed to the substructure at around 103.3 eV in the case of the plasma deposition of fluorinated precursor. The higher silica concentration of SiO_x thin film (i.e. the deposition from HMDSO/O₂ and TMCTS/O₂), compared to that of the fluorinated SiO_xC_yF_z film, is explained by the lower C/Si ratio. Furthermore, higher X₃-SiO and X₂-SiO₂ bond contents are observed in the FTEOS/O₂ thin film, higher than those in the FTEOS/O₂/TMCTS copolymer. This result is in agreement with the higher carbon concentration in the fluorinated homopolymer compared to its copolymer.

Table 3 Percentages and assignments of the different components present in high resolution O_{1s} and Si_{2p} peaks of films deposited from HMDSO/O₂ (1/5), TMCTS/O₂ (1/5), FTEOS /O₂/TMCTS (1/4/4) and FTEOS/O₂ (1/1) (*P* = 100 W, *p* = 0.02 Torr, *t* = 2 min)

	O 1s			
	X-SiO ₃		SiO ₄	
	BE (eV)	%	BE (eV)	%
HMDSO/O ₂	532.2	90.0	533.3	10.0
TMCTS/O ₂	532.7	82.8	533.8	17.2
FTEOS/O ₂ /TMCTS	532.4	86.0	533.2	14.1
FTEOS/O ₂	532.4	80.6	533.9	19.4

	Si 2p					
	X ₃ -SiO, X ₂ -SiO ₂		X-SiO ₃		SiO ₄ , -SiF	
	BE (eV)	%	BE (eV)	%	BE (eV)	%
HMDSO/O ₂			102.6	70.4	103.3	29.6
TMCTS/O ₂			102.7	69.2	103.4	30.8
FTEOS/O ₂ /TMCTS	101.0	12.4	102.2	71.4	103.4	16.2
FTEOS/O ₂	101.7	82.5	102.5	14.5	103.3	2.6

III.2. Influence of the plasma parameters on chemical structure of the different SiO_x- like films

The chemical structure of organosilicon homopolymer deposited from HMDSO, TMCTS and FTEOS plasmas with the addition of O₂ was characterized by FTIR spectroscopy and wettability measurements when varying the discharge power, the oxygen proportion and the

duration. The density of SiO_x and $\text{SiO}_x\text{C}_y\text{F}_z$ layers will be qualified by the shifting of $\nu\text{Si-O}$ vibration band as a function of the influence of the discharge power, oxygen addition and deposition duration on the film structure alterations and the transition from organic to inorganic nature. Therefore, the conditions of the copolymer elaboration were chosen in function of the corresponding homopolymer elaboration: TMCTS homopolymer containing low carbon content and FTEOS homopolymer preserving the SiF bond.

Discharge power

This parameter is representative of the energy supplied to the system and the number of electrons injected for the dissociation and the ionization of the precursor molecules. In order to study the influence of discharge power on the structure of deposited layers, the HMDSO/ O_2 (1/5), TMCTS/ O_2 (1/5), FTEOS/ O_2 (1/1) normalized FTIR spectra were recorded for different injected power. Since the increase of the discharge power did not induce the appearance of new bands in FTIR spectra of the different deposits, the study was only focused on the dependence of the SiO_x structure versus the discharge power thanks to the evolution of the stretching band position (from 1035 - 1068 cm^{-1}) [4,19,20] (Fig. 2).

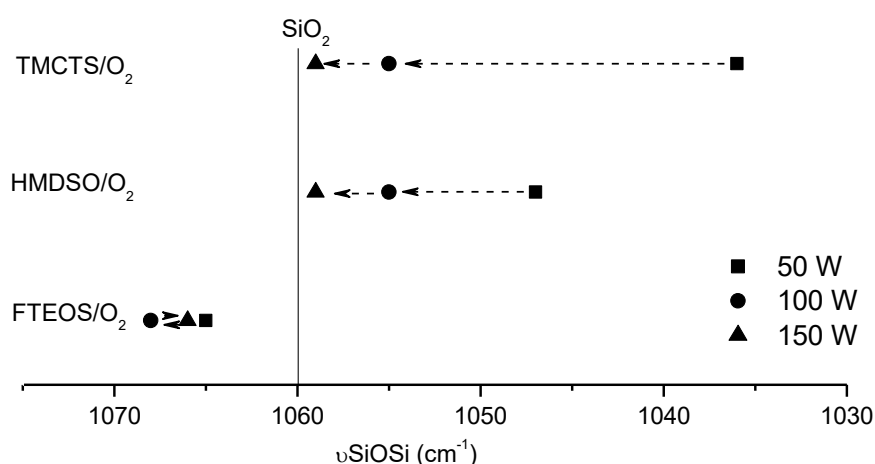


Fig. 2
Influence of the
discharge

power on the wavenumbers of the Si-O-Si vibration band of HMDSO/ O_2 (1/5), TMCTS/ O_2 (1/5), FTEOS/ O_2 (1/1) films at $t = 2$ min

According to the literature [19,27], with the power increasing, the hydrocarbon bonds of the organosilicon layers split to form the SiO_x layers. Therefore, the increase in the injected power should have a significant effect on νSiO band. Indeed, for the two precursors of SiO_x layer, the power increase from 50 W to 150 W makes possible the growth of a denser SiO_x layer since the SiO stretching band position at 1047 cm⁻¹ and 1036 cm⁻¹ for HMDSO/O₂ (1/5) and TMCTS / O₂ (1/5) thin film, respectively, shifts to 1059 cm⁻¹. The dependence of the cyclic precursor on discharge power (if lower than 100 W) is more pronounced. It might be explained by a threshold energy (here 100 W) for disintegrating the cyclic structure, to form random structure of SiO₂-like network.

In the case of FTEOS/O₂, the band position seems to be less altered with the increase of discharge power. This means that in the studied power domain, the network structure of the fluorinated SiO_xC_yF_z is independent to the discharge power. This fact can be explained by the bond energy of Si-F which is higher than Si-O, O-C and C-C [14]. Thus, Si-F bond is less degraded and the network of FTEOS/O₂ film remains in a more relaxed state.

Oxygen addition

As one can see from Fig. 3, with the increase of oxygen proportion, the SiO stretching band position of HMDSO/O₂ and TMCTS/O₂ shifts from around 1040 cm⁻¹ to 1057 cm⁻¹ and 1060 cm⁻¹ respectively, leading to the conclusion that the SiO_x structure network becomes more and more inorganic. Once again, the effect is emphasized with the cyclic structure. Such a behavior could be explained by higher SiO/SiC ratio in monomer cyclic structure (8/4) compared to the linear one (2/6). So, HMDSO monomer needs more oxygen quantity for oxidizing hydrocarbon groups than TMCTS in order to approach the inorganic network. On the contrary, increasing the oxygen proportion in the plasma phase does not influence the network structure of SiO_xC_yF_z layer since Si-O stretching band position remains located around 1067 - 1070 cm⁻¹ whatever the O₂ proportion. This is also explained by the stability and the high Si-F

energy bond. Due to the stable SiF bond, fluorinated FTEOS/O₂ layer network is less influenced by the oxygen addition, so the network is always the most relaxed.

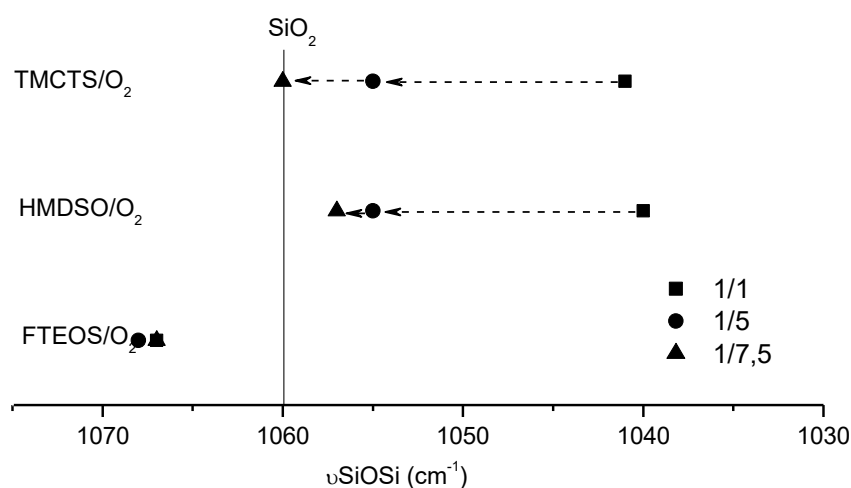


Fig. 3 Influence of the precursor/O₂ ratio on the wavenumbers of the Si-O-Si vibration band of HMDSO/O₂, TMCTS/O₂, FTEOS/O₂ films at $P = 100$ W, $t = 2$ min

The addition of oxygen as a reactive gas in the process of plasma polymerization allows to easily reduce hydrocarbon elements in the deposit, and to contribute to the crosslinking increase [7,33-35]. Indeed, molecular oxygen dissociates to form atomic oxygen, known as a polymer degradation agent. The increase in the oxygen concentration in the plasma phase also induces an oxidation of the growing layer and therefore an increase in the hydrophilicity of the

film surface marked by a decrease in the water contact angle (WCA), from 51 ° to 35 ° for HMDSO/O₂, from 74 ° to 33 ° with the TMCTS/O₂, and from 53 ° to 13 ° for FTEOS/O₂ (Fig. 4).

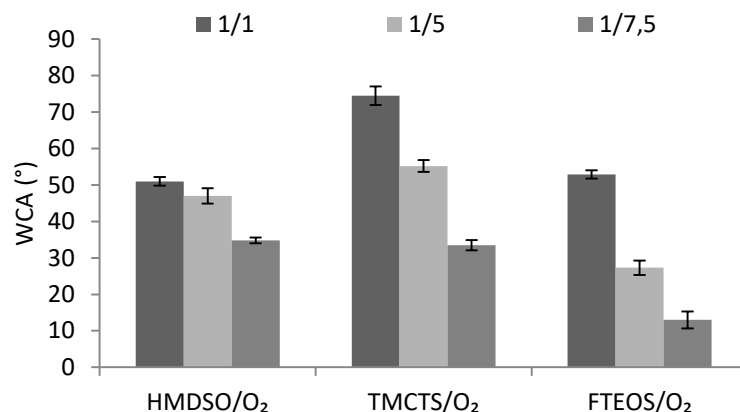


Fig. 4 Influence of the precursor/O₂ ratio on the wettability of HMDSO/O₂, TMCTS/O₂, FTEOS/O₂ films at $P = 100 \text{ W}$, $t = 2 \text{ min}$

With increasing the oxygen concentration in the gas mixture, fragmented oxygen species started interacting with organosilicon molecules in plasma phase. Fragmented species are further oxidized by oxygen plasma species interacted with carbon species on the surface. Oxidation of carbonated species resulted in removal of methyl groups and formation of volatile products, such as CO, CO₂ and H₂O, which helps in the elimination of hydrophobic species from the surface. So, in the case of oxygen concentration increase in the gas mixture, organosilicon thin film becomes more inorganic in the bulk and more hydrophilic on surface. The FTEOS /O₂ layer is even more hydrophilic than that of HMDSO/O₂ and TMCTS/O₂. This can be explained by the presence of -OH bond detected by FTIR spectroscopy (at 3440 cm⁻¹, Fig.1).

Deposition duration

For two non-fluorinated homopolymers, the increase of the deposition time induces a slight shift of the SiOSi band position to higher wavenumbers (from 1055 cm⁻¹ to 1059 cm⁻¹ and from 1051 cm⁻¹ to 1057 cm⁻¹, for TMCTS/O₂ and HMDSO/O₂, respectively) (Fig. 5).

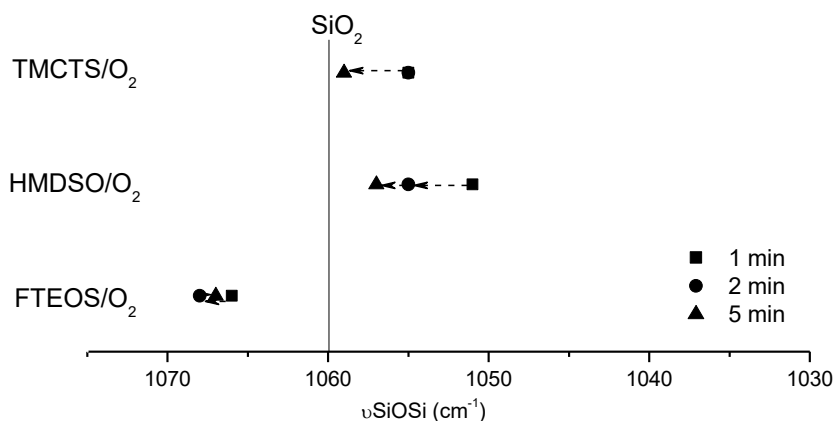


Fig. 5 Influence of the deposition duration on the wavenumbers of the Si-O-Si vibration band of HMDSO/O₂ (1/5), TMCTS/O₂ (1/5), FTEOS/O₂ (1/5) films at $P = 100$ W

ν SiO position of FTEOS/O₂ shifts to around 1066 cm⁻¹ and 1068 cm⁻¹ when the deposition duration increases from 1 min to 5 min, respectively. This means that as expected this parameter does not alter too much the chemical structure of the layers. Thus, the hydrophilicity of SiO_x surfaces remains almost constant as noticed in Fig. 6. Surface property of non-fluorinated films seems to be preserved with increasing of the deposition duration, probably because of polar surface group saturation. In the case of the FTEOS/O₂ film deposition, when the deposition time varies from 1 min to 5 min, the WCA is decreased from 59 ° to 38 °. The FTEOS/O₂ polymer surface becomes more hydrophilic. Such a decrease with increasing the duration may be explained by an excessive radical formation at the top monolayer due to the fluorine atom plasma-etching, followed by fast post-oxidation of this monolayer non-detectable with FTIR and XPS spectroscopies since the wettability measurement is the most surface-sensitive technique.

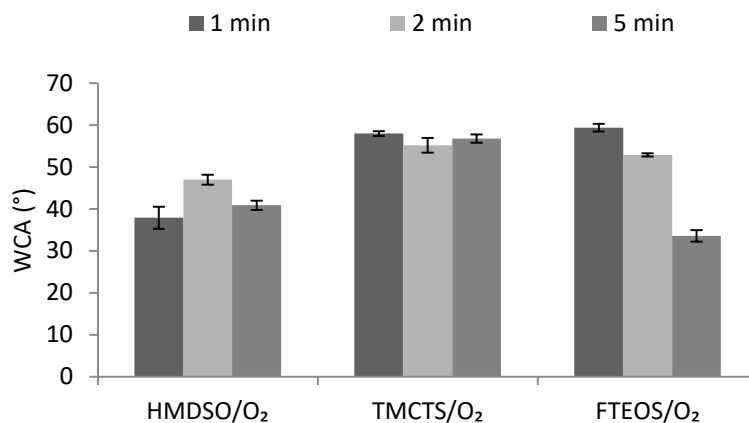


Fig. 6
the deposition
wettability of

Influence of
duration on the
HMDSO/O₂

(1/5), TMCTS/O₂ (1/5) and FTEOS/O₂ (1/5) films at $P = 100$ W

III.3. Aging of SiO_x and SiO_xC_yF_z layers

The stability of silicon thin film was studied by following the evolution of film wettability (i.e. surface and bulk changes). Films deposited on PC substrates and glass slides were aged at reduced or atmospheric pressure and were analyzed by FTIR and WCA measurements.

Wettability

During the aging process, all types of silicon dioxide and fluorinated silicon dioxide plasma-films stored at reduced or at atmospheric pressure showed the same increasing of the WCA values whatever the support - PC film or glass slide. Fig. 7 presents the case of TMCTS/O₂ film. As one can see, after the plasma deposition, films surface is less hydrophobic compared to neat PC (WCA = 82 ± 2 °) but more hydrophobic than Ar plasma-pretreated PC (WCA is around 38 ± 1 °). Under reduced pressure, the contact angle presents a fast increase from 55 ± 2 ° to 83 ± 1 ° and from 55 ± 1 ° to 84 ± 2 ° on PC and glass slide coated surfaces, respectively. At atmospheric pressure, the maximum value of WCA is about 65 ± 1 ° and 68 ± 1 °, in case of PC and glass slide substrates, respectively. In all cases a plateau is observed after 15 days of aging. The same plateau value for TMCTS/O₂ thin films deposited on PC and glass slide substrates stored under two aging conditions demonstrated that WCA change is not caused by the migration of additives from plastic substrate into organosilicon thin film.

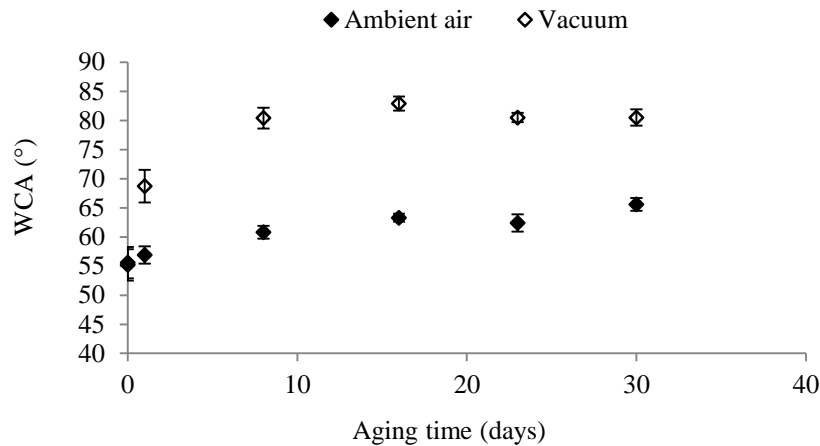


Fig. 7 Influence of the ageing duration on the water contact angle with water for TMCTS/O₂ plasma film ($P = 100$ W, $t = 2$ min, $r = 1/5$) stored under reduced or atmospheric pressure

WCA measurements for all films were also performed after 30 days of aging, and the data are gathered in Table 4 as the difference between the contact angle, i.e. the difference between the plateau value (at $t = 30$ j) - the initial one (at $t = 0$ j).

Table 4 Differential wettability between 0 and 30 days of aging for films deposited from HMDSO/O₂ (1/5), TMCTS/O₂ (1/5), FTEOS /O₂/TMCTS (1/4/4) and FTEOS/O₂ (1/1) ($P = 100$ W, $p = 0,02$ Torr, $t = 2$ min)

Δ WCA	HMDSO/O ₂	TMCTS/O ₂	FTEOS/O ₂	FTEOS /O ₂ / TMCTS
Atmospheric pressure	13.7	10.4	8.0	13.2
Reduced pressure	30.1	27.6	24.2	20.0

For all plasma-treated films, the Δ WCA is positive meaning that the surfaces become more and more hydrophobic. Besides, the Δ WCA value is always higher for samples stored at reduced pressure than for samples stored at atmospheric pressure. Such a decreasing of the hydrophilicity is known as the hydrophobic recovery. This phenomenon is assigned to a variety of physical and chemical processes, including: re-arrangement on chemical groups of the surface exposed to plasma treatment; oxidation and degradation reactions at the surface; diffusion of low molecular weight products from the outer layers into the bulk of the polymer; plasma-treatment induced diffusion of additives introduced into the polymer from its bulk toward its surface [36,37]. Samples stored at atmospheric pressure are less hydrophobic than those aged under reduced pressure (Fig. 7), This phenomenon is even more pronounced with

the initially hydrophobic FTEOS deposit. Such a behavior may be promoted by the absorption of water molecules present in the atmospheric air, the so-called plasticizing effect leading to an increase of the free volume and swelling of the polymeric layer enhancing the chain mobility. These hydrophobic chains turn over towards the air that reduces the aging rate [38-40].

Influence of the ageing on the chemical structure of the deposited layers

The comparison of the FTIR spectra (not shown here) of as-deposited and aged films after 15 days storage in air shows some alterations summarized as follows: shift of the Si-O-Si band position from 1055 cm^{-1} (for TMCTS/O₂, HMDSO/O₂, FTEOS/O₂/ TMCTS films) and 1068 cm^{-1} (FTEOS/O₂) to around 1060 cm^{-1} , increase of its intensity, appearance of the band assigned to silanol Si-OH bending vibration bond at 935 cm^{-1} , evolution of the intensity of the hydroxyl-bonded Si-OH groups at 3350 cm^{-1} . Therefore, one may conclude that these layers are aged. The results of these bulk analysis are inconsistent with the results obtained with the corresponding surface analysis (i.e. by the wettability measurements) since it is shown that silanol groups are hydrophilic. The only explanation of these experimental results can be the plasticization effect in the overall film thickness. The total film composition becomes more polar because of the silanol formation while the surface remains or starts to be more hydrophobic due to the increase of the free volume and the turnover of any formed polar groups. Such hypothesis should be verified by a more relaxed network presence after ageing.

Therefore, the ageing of the different layers was also accompanied by the displacement of the band maximum according to the chemical nature of the aged layer (Fig. 8). After 5 days of aging, for the non-fluorinated organosilicon homopolymer, the wavenumber of the Si-O vibration band increases from 1055 cm^{-1} to 1064 cm^{-1} while it decreases to 1058 cm^{-1} for the fluorinated homopolymer. It can be noted that the maximum of the νSiO vibration and the maximum of the vibration band of the fluorinated layer tend towards 1060 cm^{-1} . According to [4,25], this value corresponds to SiO₂-like structure. The result could be explained by intrinsic

surface restructuring via reorientation of the polar functional part towards surface during the hydrophobic recovery. This phenomenon allows introducing hydrophilic polar functional groups into polymer bulk, thus leading to the formation of SiO₂ network.

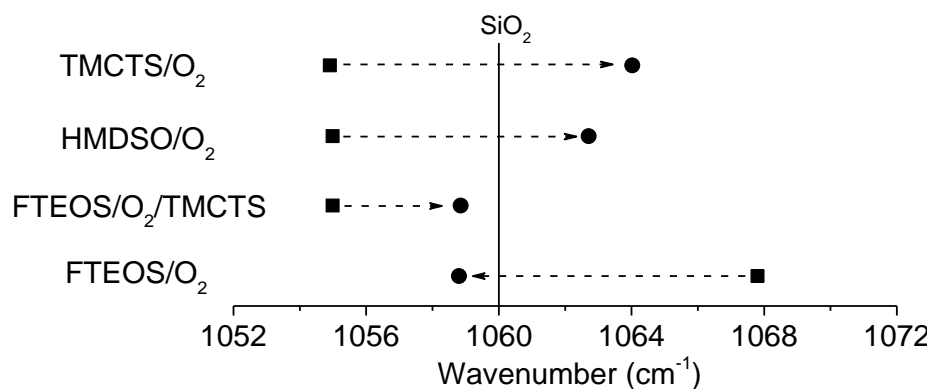


Fig. 8 Shifting of Si-O-Si band position of as-deposited and 5th days for HMDSO/O₂ (1/5), TMCTS/O₂ (1/5), FTEOS/O₂/TMCTS (1/4/4) and FTEOS/O₂ (1/1) deposited at $P = 100$ W, $t = 2$ min stored at atmospheric pressure.

III.4. Barrier properties

Water permeation kinetics are measured on neat and plasma-treated PC supports. The impact of the different coatings is analyzed through the barrier improvement values which are calculated by the ratio between permeability coefficient for the coated PC substrate and permeability coefficient for the neat PC substrate (Table 5).

Table 5 Stoichiometry, WCA, water and oxygen transport properties on the untreated and plasma coated PC film

	Permeability coefficient (Barrer)		Barrier improvement factor (%)		Stoichiometry	WCA (°)
	H ₂ O	O ₂	H ₂ O	O ₂		
PC	1036 ± 32	1.93	-	-		82 ± 2
+ TMCTS/O ₂ (1/5)	856 ± 63	0.38	18	80	SiO _{1.5} C _{0.1}	55 ± 2
+ HMDSO/O ₂ (1/5)	888 ± 73	0.67	14	65	SiO _{1.3} C _{0.1}	47 ± 1
+ FTEOS/O ₂ /TMCTS (1/4/4)	993 ± 20	0.64	5	67	SiO _{1.4} C _{0.8} F _{0.1}	59 ± 1
+ FTEOS/O ₂ (1/1)	1159 ± 69	0.81	-	58	SiO _{1.5} C _{1.5} F _{0.1}	53 ± 1

Water barrier properties of PC substrate are improved by the plasma-silicon coating, except in the case of FTEOS/O₂ film. Barrier improvement factor slightly increases for FTEOS/O₂/TMCTS film (5 %) and significantly increases for TMCTS/O₂ and HMDSO/O₂ films (18 % and 14 %, respectively). Fluorinated homopolymer which has a high value of C/Si, and O/Si ratio (= 1.5) (Table 2) does not present barrier effect to liquid water. On the other hand, all four silicon thin films reveal the improved oxygen barrier properties of PC substrate. The highest improvement factor of O₂ is 80 % in case of TMCTS/O₂. HMDSO/O₂ and FTEOS/O₂/TMCTS coating show a similar O₂ barrier improvement at 65 - 67 %. The fluorinated silicon thin film is less barrier towards O₂ permeation with only 58 % of improvement. Therefore, the inorganic SiO_x coating are much more efficient than the organic ones to increase the water liquid barrier property. Indeed, TMCTS/O₂ coating which has high inorganic and dense SiO_x structure is identified as the most efficient for barrier property improvement. Fluorinated SiO_xC_yF_z copolymer even with a moderate hydrophobic character and the lowest density shows barrier properties towards liquid water. In packaging industry, the deposition of silicon oxide on polymer thin film is of increasing interest in order to prevent the permeation of different gases like oxygen and carbon dioxide, or water (vapour) through the material. The oxygen transport properties of the SiO_x coatings deposited from mixture of HMDSO/O₂ on poly(ethylene terephthalate (PET), low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP) films obtained by using cold plasma technology were studied [7,41-43]. It is found that SiO_x coating can enhance the oxygen barrier property of the packaging films more than 13% compared to uncoated films. Therefore, the results obtained in the present work (Table 5) testify to the promising choice of the plasma precursors.

IV. Conclusion

In this study, silicon-derived and fluorocarbonated silicon-derived (SiO_x and $\text{SiO}_x\text{C}_y\text{F}_z$) layers were deposited on polycarbonate (PC) substrate from hexamethyldisiloxane (HMDSO), 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS) and fluorotriethoxysilane (FTEOS) in presence of oxygen by plasma enhanced chemical vapor deposition. The inorganic SiO_x type deposit demonstrates higher density in comparison with $\text{SiO}_x\text{C}_y\text{F}_z$ type by less relaxed Si-O-Si angle, high O/Si ratio and low carbon concentration in film structure. It was demonstrated that the permeation properties of the deposited films are more strongly dependent on the film density than on the surface chemistry. Moreover, a small variation of hydrophobicity does not change the permeability of plasma-deposited materials.

The influence of the plasma parameters (oxygen addition, discharge power, deposition duration) on the film properties is studied in order to control the SiO structure and the surface hydrophobic-hydrophilic balance. Inorganic character of SiO_x -derived layers is found to be enhanced with increasing of O_2 concentration in the gas mixture and the discharge power, while the carbon concentration in $\text{SiO}_x\text{C}_y\text{F}_z$ film can be reduced with a longer deposition duration. The aging of organosilicon layers was studied. The related mechanism in air or under reduced pressure is based on the "hydrophobicity recovery" enhanced by a plasticization effect due to water absorption inducing deformation of the layer structure. TMCTS/ O_2 was found as the best coating to enhance the water barrier properties of PC substrate. The barrier improvement factor of 18 % was obtained in this case.

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