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Plasma and surface diagnostics in PECVD from silicon containing organic monomers

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Abstract: Advances are presented in the study of chemical composition, properties and deposition mechanism of thin films deposited via RF glow discharges fed with oxygen and/or silicon-containing organic monomers. The effect of substrate temperature, ion-bombardment, and feed O_2/monomer ratio are described. A general deposition mechanism is proposed.

INTRODUCTION

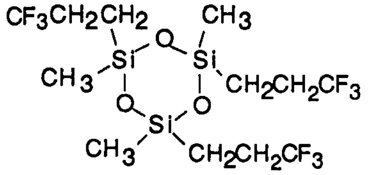
Silicon-containing organic compounds (organosilicons) are used as *monomers* in low-pressure plasma deposition of silicone-like and silicon oxide thin films, due to their availability, liquid state, volatility at room temperature, safe handling, and low cost. By choosing a suitable monomer and/or by changing the feed oxygen content, a wide range of materials can be obtained, which match performances required in different technological arenas. The chemistry of the deposits can be, in fact, tuned from silicone-like, where the organic moiety (C, H content) of the film is of relevance, to SiO2-like inorganic coatings of completely different chemistry and properties. Many potential applications exist for these films in microelectronics (dielectric layers), optics (hard transparent coatings), food packaging and fuel transport (gas, vapor, and liquid diffusion barrier films), biomedical engineering (inert coatings, low-energy surfaces), and corrosion-weathering protection (passivating layers) **(1-7)**.
Plasma-polymerized (PP-) organosilicons are deposited through homogeneous and heterogeneous elemental steps, where film precursors, and other species (charged particles, etchants) generated in the glow, play different roles in plasma-surface interactions **(1,8-14)**. The use of non-intrusive, *in situ*, diagnostic techniques is of paramount importance in the study of those processes. Moreover, *in situ* diagnostics have to be used in order to fully characterize the effects of the experimental parameters for each deposition system, in order to customize films for applications, and to easily scale-up from laboratory research to industrial protocols.

EXPERIMENTAL SECTION

The monomers listed in Table 1 have been used either alone, with argon as a carrier, or in a mixture with oxygen. In each case 13.56 MHz RF glow discharges were performed at 100 mtorr pressure, and 0.1-0.4 watt/cm^2 power density. Under these conditions the nucleation of powders in the glow was minimized. The total flow rate was kept constant (5-30 sccm) in each set of experiments; substrate temperature and bias were controlled. It is worth noting that the monomer TFC contains fluorine in its cyclosiloxane structure. Home-made steel parallel plate reactors have been utilized; in particular, a triode configuration **(8,15)** was employed to study the effect of positive ions hitting the growing films from the plasma. The energy of the ions was tuned by varying the RF bias applied to a third substrate-holder electrode by means of a second 13.56 MHz generator.

Actinometry (16-18) was used to check that no difference arose in line intensities of emitting species when bias was applied. In this way the energy of the ions was tuned *without changing the plasma species density*, thus disentangling the physical contribution of ions from the chemical one of neutrals to the deposition process.

TABLE 1 monomers

formula	name	acronym
$Si(CH_3)_4$	Tetramethylsilane	TMS
$Si(OCH_2CH_3)_4$	Tetraethoxysilane	TEOS
$3(CH_3)Si\text{-}NH\text{-}Si(CH_3)_3$	Hexamethyldisilazane	HMDSN
	2,4,6 tris [(3,3,3 trifluoropropyl) (methyl)] cyclotrisiloxane	TFC

A reactor interfaced *in vacuo* to an Electron Spectroscopy for Chemical Analysis (ESCA) spectrometer allowed us to perform surface analysis just after film deposition, and to study their oxidation under controlled oxygen exposure, thus avoiding external contaminations. This diagnostic approach, called *in situ* ESCA, was proved to beparticularly useful for studying PP-TMS films (8,11,14,19). The film hydrogen content was studied by means of FT-IR spectroscopy. Table 2 summarizes the diagnostics and the experimental approaches utilized.

Actinometry and Mass Spectrometry (MS) of the exhaust gas were utilized as plasma diagnostics. Emission Spectroscopy of organosilicon fed glows reveals only emitting species such as H, and Si atoms, CH and SiH radicals; O atoms, OH radicals, and CO molecules are present when O_2 is added (20-22). Since those species could hardly be related to the monomer, or to the *real* film precursors in a deposition mechanism, this technique loses its diagnostic power for this kind of discharge. By using actinometry, however, it is still possible to derive the monomer fragmentation pattern, to probe the electron density as a function of the feed composition, or to check the influence of the bias applied to the substrate.

MS analyses of monomer/Ar mixtures in plasma-on and plasma-off conditions reveal the presence in the plasma of unreacted monomer, hydrogen and hydrocarbons as stable products, and fragments corresponding to monomer units without either methyl groups or hydrogen atoms, or both. Oxidized hydrocarbons and organosilicons are present when O_2 is added to the discharge (1,10,12,23,24). MS has been used to calculate the monomer conversion in volatile products and film, as a function of the feed O_2/monomer ratio.

TABLE 2

Aspect under investigation	Diagnostics techniques and experimental approaches
Homogeneous reactions	Actinometry, Mass Spectrometry
Ion-bombardment	Substrate RF-bias tuning, Actinometry
Chemistry	ESCA, Transmission FT-IR
Post-deposition reactivity	*in situ* ESCA, Transmission FT-IR, *in situ* Laser interferometry
Deposition rate and density	Gravimetric Analysis, Profilometry
Hardness	ASTM D3363 "pencil test"
O_2 permeability	O_2 permeameter

RESULTS AND MECHANISMS

Film composition and properties depend on the chemical reactions in the plasma and on the film surface, as well as on surface events (radicals quenching, rearrangements, oxidation, contamination) occurring after the film exposure to the atmosphere. In this section we show the effects of substrate temperature, bias and O_2/monomer feed ratio on deposition rate and composition of PP-TMS, -TFC, -HMDSN, and -TEOS films. The first two effects are discussed for glows fed with monomer and Ar at a fixed ratio, the last refers to glows fed with constant total and monomer flows, but with variable O_2 and Ar flows.

Substrate bias and temperature do not alter plasma composition, rather, they control the adsorption of species on the growing film, the surface polymerization of its precursors, the film etching and its pyrolysis. On the other hand, the addition of O_2 to the glow dramatically alters plasma chemistry and precursors distribution, increasing monomer conversion in deposit and fragments, and decreasing film deposition rate and organic character. Plasma and film diagnostics of monomer/Ar glows show a strong monomer fragmentation even when film stoichiometry is "monomer-like". New and/or different signals are in fact obtained in film FT-IR spectra, and C1s ESCA spectra are different from those expected on a monomer structure retention hypothesis (1,8-15).

In order to simplify kinetic hypotheses, it is useful to define two classes of film precursors: those which contain silicon, or "inorganic" fragments, and those which do not, the "organic" ones. Under any experimental conditions, the composition of the deposits, *i.e.* their organic and inorganic character, mirrors both the distribution of precursors and the extent of plasma-surface interactions.

Plasma-surface interactions: effect of substrate temperature and bias

Temperature influences elemental reactions and equilibria involved in plasma-surface interactions. An increase in temperature decreases film growth rate, as shown in figure 1A, and leads to denser (8,26), crosslinked deposits with reduced carbon and hydrogen content (1,8-15). PP-TMS films deposited under those conditions by TMS/Ar feeds are oxidized to a lesser extent by the atmosphere (11,19). PP-HMDSN, -TEOS, and -TFC do not show any relevant oxidation after atmospheric exposure.

The bias-induced ion bombardment can enhance or depress the deposition rate of PP-organosilicons, as shown in figures 1B and 1C, depending on ion energy, but also on film structure; furthermore, the higher the bias, the lower the film organic content.

The effects described so far can be explained assuming the *Activated Growth Model* of Scheme I as a general, simplified deposition mechanism; two competing processes are triggered by ions of different energy (8,15,22), as will be explained. The same model was successfully utilized to explain the chemical kinetics of plasma-deposited fluoropolymers (18,27), and it is proposed as a general deposition mechanism for plasma-deposited thin films.

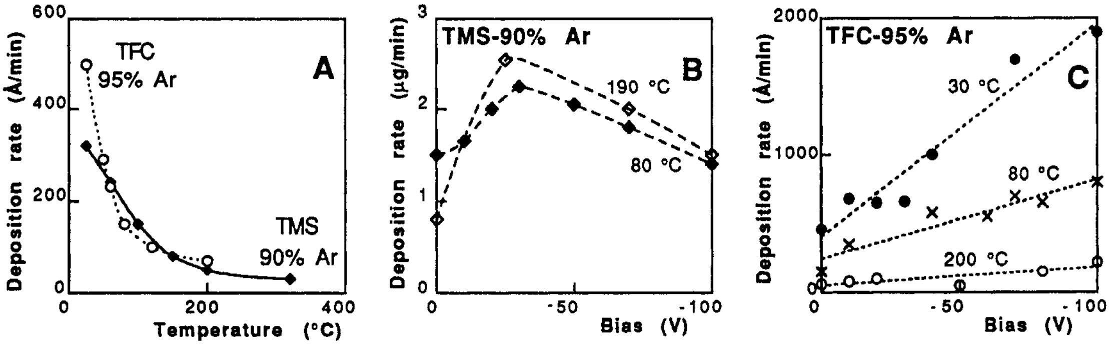


Fig. 1 Deposition rate of: **(A)** PP-TMS and PP-TFC *versus* substrate temperature; **(B)** PP-TMS, and **(C)** PP-TFC *versus* substrate bias.

Scheme I: Activated Growth Model

monomer $\xrightarrow{\text{e-impact}}$ organic fragments + inorganic fragments	A
organic and inorganic fragments *(PLASMA)* $\rightleftarrows$ organic and inorganic fragments *(SURFACE)*	B
film surface $\xrightarrow[\text{(LOW ENERGY)}]{\text{ion-impact}}$ surface active sites	C
organic and inorganic fragments *(SURFACE)* + surface active sites $\longrightarrow$ film	D
film + etchant species $\xrightarrow[\text{(HIGH ENERGY)}]{\text{ion-impact}}$ film (more inorganic) + volatile species (CO, CO_2, H_2O, etc.)	E
film $\xrightarrow[\text{(HIGH TEMPERATURE)}]{\text{pyrolysis}}$ film (more inorganic) + volatile species (CO, CO_2, H_2O, etc.)	F

Step **A** describes the generation of film precursors, which undergo heterogeneous and homogeneous reactions. Steps **B** and **C**, namely adsorption-desorption equilibrium and film activation, are greatly influenced by surface temperature and bias, and prelude the film growth through surface polymerization of precursors (step **D**). Equilibrium **B** is shifted toward the desorption side by increased temperature, due to its negative enthalpy (**18**), and also by the increased ion energy. Low-energy ions enhance film growth rate by creating active sites (dangling bonds, distortions) for precursors adsorption, while high-energy ions depress precursor adsorption and/or trigger its ion-assisted etching (step **E**), thus decreasing the overall deposition rate, as also reported for different Si-containing plasma-deposited materials (**28,29**). Step **F**, film pyrolysis, becomes important at high substrate temperature; it depresses the deposition rate, and affects film composition.

Figure 2A shows how the increased ion-bombardment results in a marked hardness increase (ASTM D3363 "pencil test") of PP-TFC films. We ascribe this property to the increased crosslinking degree in high-bias deposited coatings, evidenced by the presence of CF and CF_2 contributions in the C1s ESCA spectra (figure 2B), which are absent in no-bias deposited films (**15**).

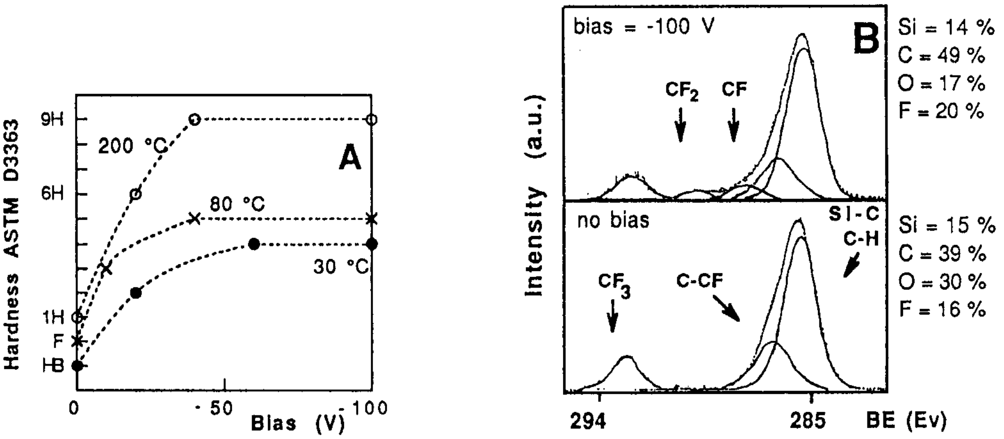


Fig. 2 (**A**) Hardness of PP-TFC films *versus* bias. (**B**) Cls spectra of PP-TFC films deposited at 80 °C in bias-on and bias-off conditions.

Effect of the oxygen/monomer feed ratio

Film growth rate and composition are functions of precursor density in the plasma; however, as shown, surface temperature and bias drive plasma-surface interactions of the species present in the plasma, influencing the deposition process. Adding O_2 to the organosilicon feed results in modifications of the monomer fragmentation pattern, due to homogeneous reactions of oxygen atoms and molecules, with the monomer and its fragments. As a consequence, density and distribution of electrons and film precursors in the plasma are alffected, thus influencing deposition rate and composition of the coatings, as will be shown.

Figure 3A shows the trends for PP-TMS, -TEOS, and -HMDSN deposition rate. Maxima, where present, are due to changes of precursors density and nature induced by O_2 addition to the feed. Increasing the O_2/monomer feed ratio leads to the ashing of the organic precursors in the plasma, lowering in this way the carbon and hydrogen content of the films (FT-IR spectra), and increasing their O/Si compositional ratio, as shown in figure 3B for PP-HMDSN. The distribution of the inorganic precursors is also modified by the plasma-ashing of their organic chains. These homogeneous reactions, which depend upon monomer and plasma conditions, determine the distribution of species in the plasma phase, which, in turn, drives deposition rate and film chemistry.

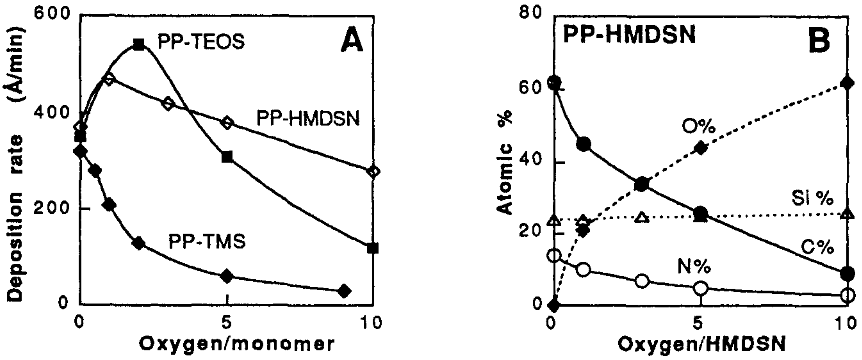


Fig. 3 **(A)** Deposition rate for PP-TMS, PP-TEOS and PP-HMDSN *versus* the feed O_2/monomer ratio; **(B)** PP-HMDSN composition (ESCA) *versus* O_2/HMDSN ratio.

Information about the homogeneous reaction pattern can be obtained by the analysis of film structure and chemistry (**1,3,8,9,13-15**), but also by plasma diagnostics. MS data presented in figure 4A show TEOS and HMDSN conversion as a function of the feed O_2 content, calculated on the basis of the behavior of different representative fragments of the monomer (**10,12**). The trends show how the monomers are more easily fragmented in O_2-containing glows, with HMDSN more sensitive than TEOS. On the basis of actinometric data (figure 4B) for Ar/O_2/HMDSN discharges (**12**), this behavior can be ascribed to oxygen-monomer and oxygen-fragment bimolecular reactions, rather than to an increased e^--impact fragmentation of the monomer. Ar emission intensity, which is proportional to the density of electrons with energy higher than 13 eV (**16-18,27**), is in fact lowered by O_2 addition, while the density of oxygen atoms is increased. The lowering of the electron density itself could be a concurrent cause for the change of the deposition rate but, in our opinion, the influence of the oxygen atoms is greater. It must be noted that oxygen atoms are almost undetected at low O_2/monomer ratio, probably because they are totally consumed in reactions with the monomer and its fragments; they are probably able to oxidize and ash the deposit only when the feed ratio is high, as suggested by other authors following afterglow experiments (**2,5,30**). Actinometric (H atoms, CH and OH radicals, CO molecule) as well as MS trends obtained using TEOS, HMDSN, and TMS as monomers (**23**) confirm the conclusions stated above, and summarized in Scheme II.

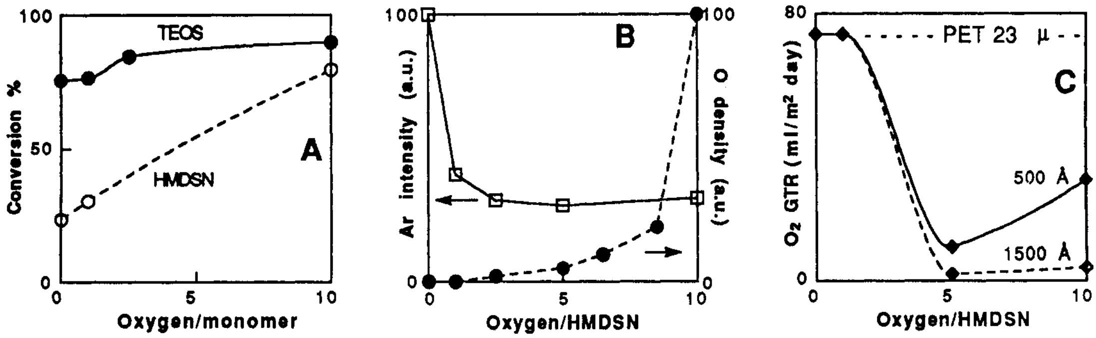
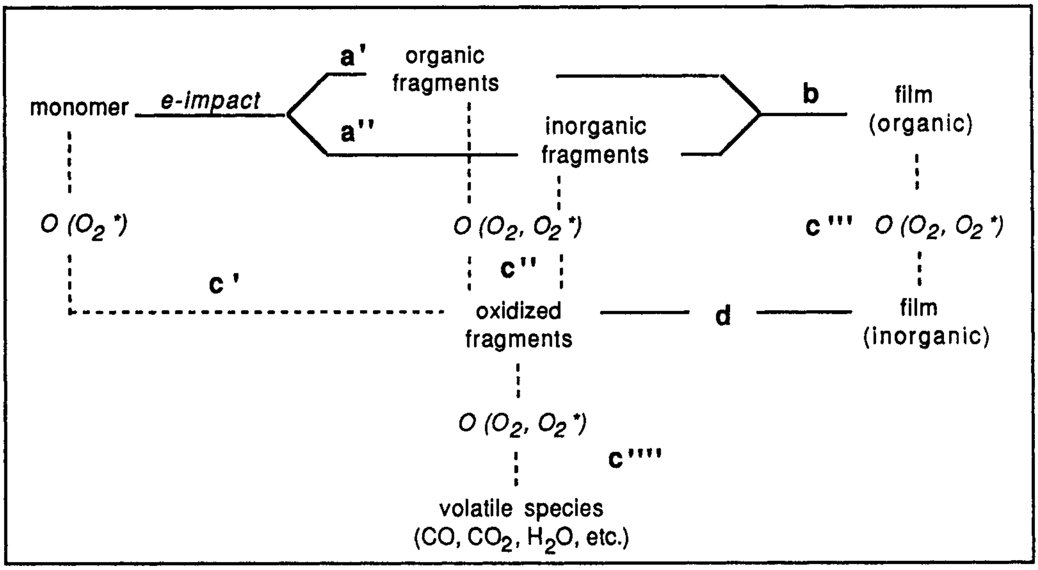


Fig. 4 **(A)** Monomer conversion for TEOS and HMDSN *versus* the feed O_2/monomer ratio; **(B)** Ar emission intensity (7503 Å), and oxygen atoms (7775 Å) actinometric density for Ar/O_2/HMDSN glows, *versus* O_2/HMDSN ratio. Ar intensity has been corrected with its partial pressure; **(C)** O_2 Gas Transmission Rate of PP-HMDSN of different thickness on PET *versus* O_2/HMDSN ratio.

PP-HMDSN deposited at high O_2/monomer ratio can be used as oxygen diffusion barrier layers on conventional polymers used for food packaging and similar applications, in analogous way as PP-TEOS films (3); figure 4C shows, in fact, how the O_2 Gas Transmission Rate (GTR) of a 23 μ thick foil of Polyethylentherephtalate (PET) is reduced by PP-HMDSN films of different thickness and composition.

Scheme II: The effect of oxygen addition to the discharge



Reactions **a'** and **a''** of Scheme II describe the homogeneous fragmentation of the monomer by electron impact; organic and inorganic precursors produced in this way lead to film deposition through path **b** (steps **B** and **D** of Scheme I). Oxygen molecules and atoms, in different states, change the balance between organic and inorganic precursors in the plasma by reacting with the monomer (step **c'**), and with the fragments (step **c''** and **c''''**), thus leading, through reaction **d**, to a more inorganic coating. The heterogeneous film oxidation step **c'''** is likely to be effective at high feed O_2 content.

The chemical modifications induced in the films by those homogeneous reactions are witnessed by their increased O/Si ratio (values higher than 2 are due to Si-OH groups) detected by ESCA, by the drastic reduction of organic functionalities such as Si-CH_x groups (FT-IR results), and by the change of properties such as permeability, as shown, **(1,3,8,9,13-15,22-25)**, and refractive index (not shown).

Figures 5A and 5B show the ESCA Si2p and C1s spectra for PP-TMS films deposited at different feed O_2/TMS ratios. When the ratio is increased, as expected, the Si2p peak moves to higher binding energies, This is due, at low ratio, to silicone-like chains $(C_x\text{-}Si\text{-}O_y)_n$ in the material and, at high ratio, only to Si-O bonds. The film carbon content is reduced, and the high binding energy region of the C1s peak (CO_x groups) enlarges.

The change in film composition, shown also by PP-HMDSN, is supported by the trends in figure 5C of the Si2p signal Full Width Half Maximum (FWHM) as a function of the feed ratio. Si2p width is narrow at ratio zero, when only carbon and hydrogen (and nitrogen in PP-HMDSN) are bound to silicon, then it increases with the ratio, due to the presence also of Si-O bonds in the film, then it narrows again when, at high ratio, the films practically contains only Si-O bonds.

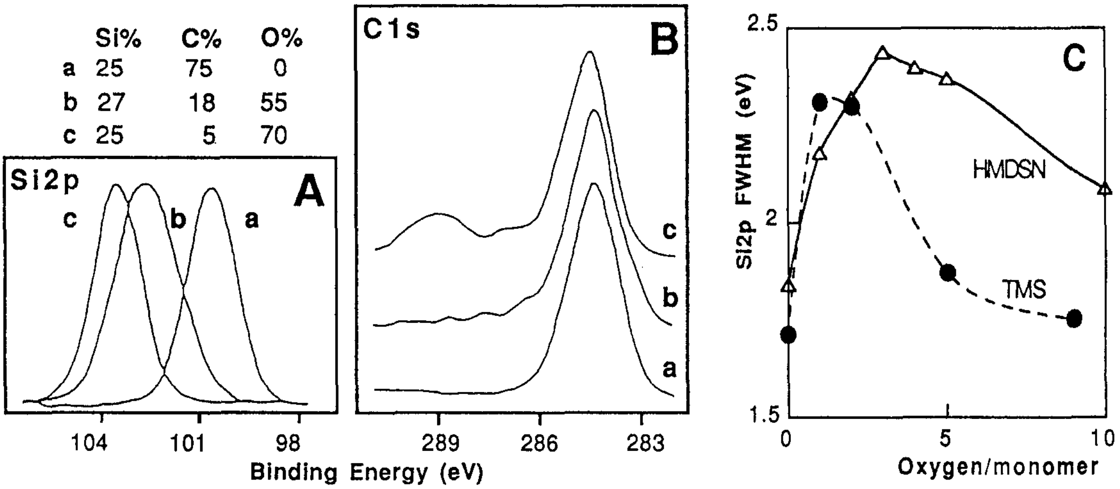


Fig. 5 **(A)** Si2p, and **(B)** C1s ESCA spectra of PP-TMS deposited at 25 °C at different feed O_2/TMS ratio: a) O_2/TMS = 0; b) O_2/TMS = 2; c)O_2/TMS = 9; **(C)** Si2p FWHM for PP-TMS and PP-HMDSN *versus* the O_2/monomer feed ratio.

CONCLUSIONS

Plasma Enhanced Chemical Vapor Deposition from organosilicon monomers allows synthesis of thin films with tailored composition and structure. Depending on substrate temperature, substrate bias, and oxygen/monomer feed ratio among process parameters, films with chemistries ranging from silicone-like to silicon-dioxide can be obtained, which can be utilized in many different technological fields. The use of proper plasma and surface diagnostic techniques is of strategic importance for studying the deposition mechanism, and for scaling-up the processes.

Due to the relevance of the diagnostics, and to the reduced power of Emission Spectroscopy, a multi-probe approach is strongly suggested for organosilicon fed glows, along with the use of techniques still not widespread in plasma and thin film chemistry. The use of analytical probes such as Laser Induced Fluorescence (LIF), Solid State Nuclear Magnetic Resonance (SS-NMR), Static Secondary Ion Mass Spectroscopy (S-SIMS), and ESCA of derivatized films promise to improve the understanding of plasma and surface reactions, film structure and chemistry.

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