

Production of Silicon Oxide like Thin Films by the Use of Atmospheric Plasma Torch

E M Ozono¹, E R Fachini², M L P Silva^{1,3}, L F Ruchko⁴ and R M O Galvão⁴

¹Faculty of Technology of São Paulo- FATECSP, SP, Brazil

²University of Puerto Rico, Río Piedras Campus, Puerto Rico, USA

³PSI-EPUSP, University of São Paulo, SP, Brazil

⁴Institute of Physics of University of São Paulo, SP, Brazil

E-mail: ozono@fatecsp.br

Abstract. The advantages of HMDS (hexamethyldisilazane) APT-plasma films for sensor applications were explored producing films in a three-turn copper coil APT equipment. HMDS was introduced into the argon plasma at four different conditions. Additional flux of oxygen could modulate the presence of organic components in the film, the composition varying from pure inorganic oxides to organo-silane polymers. Oxygen promoted deposition rates as high as 900 nm/min on silicon, acrylic or piezoelectric quartz crystal substrates. Films with a clustered morphology and refractive index of 1.45 were obtained, mainly due to a silicon oxide structure. Raman spectroscopy and XPS data showed the presence of CH_n and amorphous carbon in the inorganic matrix. The films were sensitive to the humidity of the air. The adsorptive capabilities of outstanding films were tested in a Quartz Crystal Microbalance (QCM). The results support that those films can be a useful and simple alternative for the development of sensors.

1. Introduction

It is well known that plasma processing can be used for a) surface modification, changing the surface wettability, adhesion, adsorption, printability, chemical reactivity, bio-compatibility, protection, sensitivity of light, etc. [1] or b) to deposit films of different kinds on a number of substrates. Those films are useful to develop microelectronic devices, as sensors and microTAS (micro Total Analysis System), because sensors require altering of small structures and the treatment of polymer surfaces is an important step in the manufacturing of many microTAS devices [2, 3].

Atmospheric plasma torch (APT) has high deposition rate of films and produces a range of film densities, being versatile compared with other available plasma equipment and processes. For instance, atmospheric plasma spray systems were used to develop NO₂ sensors and negative temperature coefficient (NTC) devices by the insertion of particles in the plasma, resulting films with various porosities [4, 5]. Aerosols also could be introduced in the film during its formation, promoting a higher degree of retention of precursor's molecular structure during the polymerization process. Problems associated with aerosols are high process pressure and the selection of the appropriate precursor which the particular partial pressure that assures high deposition rate without significant particle formation. Particle formation is a drawback on uniformity or, on the other hand, a strategy to

¹ To whom any correspondence should be addressed.



obtain composites. Thus, dense films to particles can be produced using a proper reactant and fine control of the plasma torch parameters. On such context, organosilicon compounds is a convenient precursor in APT processes because they avoid particle generation, being possible to obtain uniform films of high porosity [6].

Production of silica layers from organosilicon compounds is common, being common precursors HMDS (hexamethyldisilazane), HMDSO (hexamethyldisiloxane) [7] and TEOS (tetraethoxysilane) [8]. Nanoparticles of 160-200 nm were obtained with the introduction of HMDS aerosol, mainly components of particles being SiC_4 , $\text{Si-CH}_2\text{-Si}$ and Si-H [9]. As previously mentioned, a transparent HMDS derived film can be deposited on polycarbonate. The film composition presented few nitrogen ($\sim 0.3\%$) and C-H, N-H, Si-C, Si-N species [3]. Guruvenket et al, employing the same precursor, produced silicon carbonitride hard coatings [10]. Tendero et al summarizes the products from HMDS in APT processes as: a) stoichiometric SiO_2 films (used to protect fibers); b) films made of Si-O with carbon impurities (resistant to base solutions); and c) pure silicon films [11].

Volatile organic compounds (VOCs) pollutants must be evaluated in environmental samples where they occur at low concentration in the presence of analytical interferences. Because of that, it is mandatory the pretreatment of the sample with retention step in some part of the microTAS device. In this situation, adsorptive thin films are very important in the development of sensors and/or microTAS for VOCs analysis. Former works presented hydrophobic HMDS polymerized films with good adhesion on several distinct substrates. Those films presented polar and non polar VOCs adsorptive properties [12, 13]. Nonetheless these films were not tested regarding water adsorption and their resistance toward VOCs exposure.

The use of APT to deposit HMDS derivative films is a common procedure. Less usual is the use of this technique to obtain reproducible adsorptive films in a well controlled and well understood system. This work explores the advantage of the easiness of plasma polymerization of organic silicon compounds in a common process APT design resulting in reproducible adsorptive films for sensors and/or microTAS development in a comprehensive way.

2. Experimental

The produced APT equipment was designed to be used for deposition of thin films; therefore, some special characteristics should be provided in order to preserve monomer structure, such as low power, three coaxial tubes to allow easiness of reactant insertion on the inner section, etc. Thus, the thermal plasma is generated with argon gas under normal atmospheric pressure. The inductively coupled plasma torch consists of a three turns RF copper coil placed at the exit of the torch, around of small three concentric quartz tubes of 6, 14, and 18 mm diameters. Argon gas was injected with a flow of 1 l/min through inner channel to compose the plasma core and second flux of 25 l/min in the outer channel so the required stabilizing tangential swirl at plasma edge. Because thermal plasma is difficult to be ionized it needs to apply a spark by Tesla coil to initiate the discharge. The efficiency of power coupling to the plasma torch is modest. Other requirements such as proper trimming of the cables within the matching box and installation of a low-pass filter with electrostatic shielding in order to reduce the reflected power were fulfilled. Many shootings of torch with plasma have been done. The adjustments at inductive torch coil with plasma resulted at 1420 V of voltage and 11.56 A of current amplitude with a good tuning at 23.47 MHz. The phase shift of 74 degree between voltage and current allowed the delivery of 1037 watts of power at coil. That indicated an enthalpy of 331 W power transferred into plasma. Figure 1a schematizes the admittance of the reactants. The carrier gas injects a controlled amount of the reactant HMDS into the plasma core through the inner channel. If cross flow is preferred, the reactant also can be injected through the outer side of torch. For this alternative, the use of air as carrier gas will favour the oxidation of HMDS molecule. If argon is used, the oxidation of HMDS molecule is not favoured. The experiments were carried out positioning the samples at different distances from the top of the glass torch. Figure 1b shows the plasma torch and a sample positioned over its top (inset).

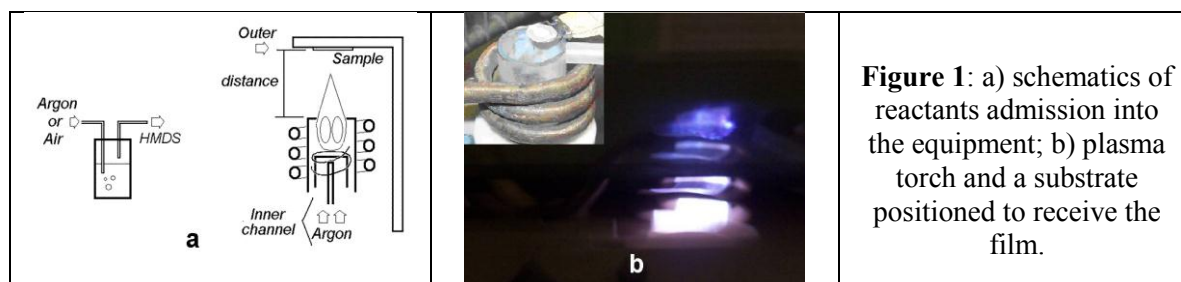


Figure 1: a) schematics of reactants admission into the equipment; b) plasma torch and a substrate positioned to receive the film.

Films were grown on four types of substrates: a) silicon wafers (used in the film's chemical and physical characterization), b) piezoelectric quartz crystal (PQC – 7 MHz, for absorptive capability assessment), c) acrylic (PMMA) (samples used in the chemical resistance evaluation) and d) polyacrylonitrile (PAN) fibers (to verify if the film grows properly and with good adherence on this material). Deionised water and P. A. grade reactants were used, except HMDS (Fluka Chemie GmbH, Switzerland) that was industrial grade.

For all tested substrates, Table 1 summarizes the four conditions used for the film growth and the resulting plasma characteristics. For each condition, 3 samples were prepared at distance of 2, 5 and 10 mm from the torch top to substrate. Since the reactant is inserted on plasma zone by a saturated carrier gas, the HMDS flow was approximately 0.5 g/min for all films that were grown under the plasma conditions during 2 minutes.

Table 1: Different conditions at APT during the growth of the HMDS films.

Condition #	HMDS injection		Carrier gas		Plasma characteristics	
	Inner channel	External channel	Argon	Air*	HMDS molecules and plasma interactions	Oxidation mechanisms
1		x	x		Low	Low
2	x		x		High	Low
3		x		x	Low	High
4	x		x	x	High	High

* Air is admitted outside of the plasma torch via an external channel

The deposition rate and refractive index were determined respectively by profilometry and ellipsometry at two wavelengths (632.8 nm and 830.0 nm). The presence of polar organic functionalities in the films was determined by infrared spectroscopy (FTIR). Raman microscopy was useful to obtain information about non polar organic residues and cluster formation. Additional chemical information came from XPS (x-ray photon electron spectroscopy). Film morphology was inspected by optical and scanning electron microscopy. Water contact angle measurements (goniometer and 4 μ L drops) evaluated the hydrophobic character of the films. The PQC setup was described elsewhere [12]. Samples of different relative humidity and VOCs content were used sequentially in order to determine the adsorptive capability of the films. Chemical resistance to VOCs was tested by contact angle measurements with organic liquids.

3. Results and Discussion

Table 2 summarizes the main results obtained by ellipsometry and profilometry measurements. Due to the plasma torch characteristics the thickness is non uniform and some samples are porous; nonetheless, high deposition rates were achieved in all deposition conditions, the highest values correspond to a film with high porosity. Thick films presented numerous clusters and their roughness makes difficult a proper measurement by profilometry. HMDS admission on the inner channel increases ion/molecule reactions and, consequently, the thickness of the films. The high refractive index observed is characteristic of films with low oxygen content. This fact suggests a low oxygen presence in the reactive space even if oxygen is admitted in the system through an external channel (deposition #4). When air is the carrier gas (deposition #3) or a low concentration of HMDS is available during deposition (deposition #1), the film obtained will have high oxygen content with a refractive index similar to silica films (~ 1.45), these conditions also lead to low deposition rates.

Table 2: Results from ellipsometry and profilometry measurements.

Condition #	Refractive index	Max. thickness (nm)	Characteristics
1	1.3 to 1.4	100	Deposition rate lower than 100 nm/min
2	~2.0	$9 \cdot 10^3$	Rough and porous films, deposition rate of 1-5 10^3 nm/min
3	1.3 to 1.4	540	Dense films, low deposition rate
4	~2.0	$3 \cdot 10^3$	Deposition rate up to ~1. 10^3 nm/min

Infrared (FTIR) measurements support the main conclusions obtained by ellipsometry and profilometry measurements; Figure 2 shows typical FTIR spectra. Common features in all FTIR spectra indicate that the films presented the species commonly found in silicon oxide films and HMDS plasma polymerization films. The strongest band corresponds to SiOSi vibration in the 1000-1200 cm^{-1} range. Other species were also found: SiCH_3 ($\sim 1250 \text{ cm}^{-1}$); CH_n ($\sim 2950 \text{ cm}^{-1}$); SiC (800 cm^{-1}) and adsorbed water (3400 cm^{-1}). Some samples prepared at a distance of 2 mm from plasma torch with condition #2 showed a weak peak at $\sim 2100 \text{ cm}^{-1}$, which corresponds to SiH. This is consistent with low quantity of oxygen and short residence time in the plasma, as discussed by Miettinen [14] in a study of silicon-carbon nanoceramics.

The FTIR SiOSi peaks show different profiles depending on the condition of film growth and they were quite different of the profile obtained by Huang [3] for a film obtained by HMDS plasma polymerization. The Si-O-Si peaks present some resemblance with bands obtained for dense silica films formed from polymerization of TEOS and tetramethylcyclotetrasiloxane (TMCTS), among other precursors [15]. As pointed out by Cui, 1000–1200 cm^{-1} region is typical for a siloxane network, occurring overlapping of peaks at: a) 1075 cm^{-1} (vibration of “fully relaxed SiO_2 -network structure with bond angle of 144° ”), b) 1100 cm^{-1} (corresponding to “larger angle Si–O–Si bonds”), c) 1150 cm^{-1} (characteristic of “highly symmetric siloxane ring structure”) and an additional peak at 1050 cm^{-1} “due to less symmetric and more random network structure” [15]. Thus, if HMDS is exposed to high plasma interaction (#2 deposition), the 1100 cm^{-1} band is privileged, probably owing to the high deposition rate that leads to disordered structure (Figure 2a) and more random configuration (Figure 2b) can occur if less reactant is present. The presence of oxygen in the plasma favours a FTIR peak profile similar to SiO_2 , as it occurs in TEOS derived plasma films. These conditions induce losses of SiCH_3 species, although some weak peak near 1250 cm^{-1} can remain (see Figure 2c), in a situation similar to Cui’s report for TMCTS, which attests the strength of such bond. Water adsorption in films can be enhanced by the presence of SiOH ($\sim 940 \text{ cm}^{-1}$) species that promotes hydrogen bonds. Although Huang had observed such species in films made from HMDS in low temperature atmospheric plasmas [3], they were not noticed in FTIR spectra in the present study. Nonetheless, the water presence (broad peak at 3400 cm^{-1}) is a good indicative of adsorptive properties of these films.

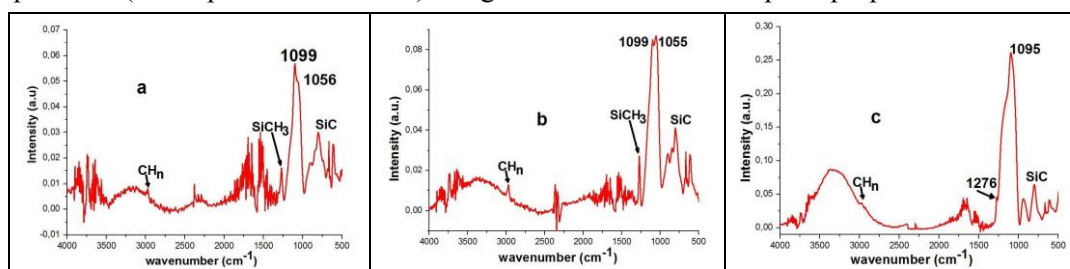


Figure 2: FTIR spectra: (#2 deposition) with a) 5 mm or b) 10 mm from the torch and c) adding oxygen (#4 deposition)

Raman microscopy can probe the small surface features that optical microscopy revealed. Raman microscopy is also capable of evaluating carbon-rich domains. Optical microscopy images show uniform films when weak HMDS-plasma species interaction are favoured (conditions #1 and #3 for the film deposition) as can be seen in Figure 3a. For these samples, weak peaks at $\sim 1450\text{ cm}^{-1}$ that correspond to CH_2 were found in the corresponding Raman spectrum. If strong interactions among

HMDS-plasma species are favoured, features can be observed in the film. If oxygen is absent in the plasma (condition #2), few graphitic domains will be observed (darker points in the centre of Figure 3b). If oxidative plasma is formed (condition #4), the number and size of these graphitic domains increase (see Figure 3c). The frequency and intensity of features increase if the film is formed closer to torch, probably as a consequence of the higher deposition rate (Figure 3, Raman spectrum).

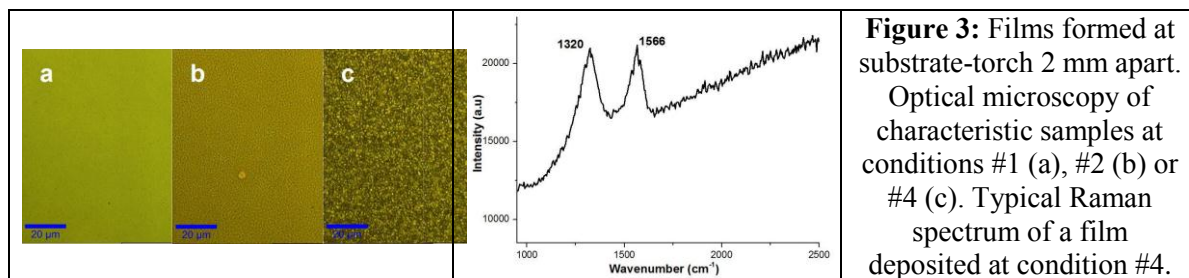


Figure 3: Films formed at substrate-torch 2 mm apart. Optical microscopy of characteristic samples at conditions #1 (a), #2 (b) or #4 (c). Typical Raman spectrum of a film deposited at condition #4.

Water contact angles were approximately 90° for all samples; organic liquids can wet these surfaces. Although these experiments pointed out to hydrophobic/organophilic species at surface, this interpretation could be inaccurate since it could also be due the roughness of the surface, as shown by SEM images, with particles approximately 1 μm long (Figure 4a). To avoid misleading, QCM measurements were performed to evaluate adsorptive properties. Samples were almost insensitive toward VOCs or water. However, samples with highest roughness (condition #4) gave intense response when exposed to a gas stream saturated in water as can be seen in Figure 4b. Probably the high porosity leads to a different phenomenon than adsorption inside the pores, such as clogging. Since these films were resistant to VOCs, they are grown on polymer substrate to test their performance as protective surface layer. Deposition on PMMA was performed without mechanical deformation of the 8-mm-thick substrate. The film was able to prevent acetone-PMMA interaction for few minutes but PMMA surface “cracks” (see detail, Figure 4c). An additional sample was prepared growing the HMDS derivative film in a mat of polymer fibres to test water adsorption in a three dimension system with increased surface area [16]. While PAN micro/nanofibers exposed to argon plasma can be severely destroyed in 15 s, the fibre mat that was protected by the HMDS derivative film showed low damage. After plasma process, a yellowish film that completely covers the fibres was obtained and can be seen in the Figure 4d. Films prepared at 2 and 10 mm apart from torch had very similar XPS spectra peaks, and they presented the same major components at similar concentrations: C: 22-25%, O: 47-44%, F: 1.6-1.5% and Si: 29%. They did not incorporate nitrogen as a film component and both had fluor, probably from a torch environmental contamination.

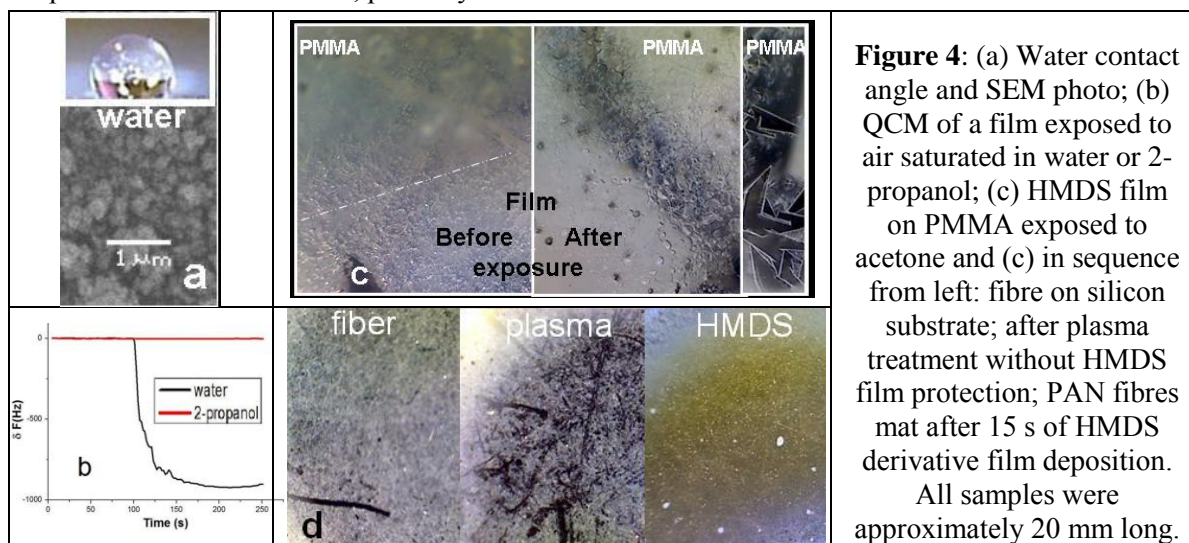


Figure 4: (a) Water contact angle and SEM photo; (b) QCM of a film exposed to air saturated in water or 2-propanol; (c) HMDS film on PMMA exposed to acetone and (c) in sequence from left: fibre on silicon substrate; after plasma treatment without HMDS film protection; PAN fibres mat after 15 s of HMDS derivative film deposition. All samples were approximately 20 mm long.

Moreover, these films presented a more defined granular morphology compared to sample prepared at 5 mm apart of the torch, which structure resembles a “sponge”. The last film had no fluor, was enriched in carbon species and impoverished in silicon oxide species when compared with its homologues. It incorporated a significant amount of nitrogen. Its composition was: C: 33%, O: 42%, N: 3% and Si: 22%. The XPS C1s peak was richer than previous films in carbonic species with oxygen and/or silicon (see arrow in the Figure 5). All of this suggests that it was formed at mild conditions in the plasma, with greater retention of the molecular structure of the precursor than its homologues films. The Si 2p peak centred at 102.9 eV vs. 103.2 eV of homologues films confirms this assumption.

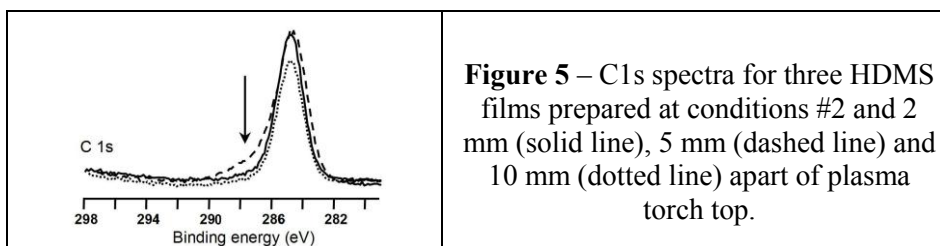


Figure 5 – C1s spectra for three HDMS films prepared at conditions #2 and 2 mm (solid line), 5 mm (dashed line) and 10 mm (dotted line) apart of plasma torch top.

4. Conclusion:

This work establishes the advantages of using HMDS derivative plasma films to construct sensors. If correct values for process parameters are chosen, it is possible to grow a film with a SiO₂ network with organic residues as Si-CH₃. The resulting film demonstrates to have excellent capability to absorb water or to protect polymer surfaces against VOCs attack.

5. Acknowledgments

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6. References

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