ELECTRICAL CHARACTERIZATION OF ADSORBENT FILMS FOR VOC'S DETECTION

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ABSTRACT

The aim of this work was the electrical characterization of HMDS and/or fluorinated plasma deposited thin films and their double layers or composites. Films were deposited on silicon wafers using homemade DC powered equipment. Electrical characterization measured the variation of capacitance as a function of voltage if films were exposed to airflow saturated with 2-propanol or n-hexane vapours. Capacitance on HMDS films changes due to exposure but a partial recovery is easily obtained using airflow. Fluorinated film has low sensitivity and double layers show retention due to reactant permeation through the fluorinated film. Composite films show intermediary behaviour and the recovery of capacitance values might be possible. Therefore, HMDS and fluorinated films are promising for sensors development. Nonetheless, whereas HMDS films seem to be useful on any capacitive sensor device, due to the difficulty in signal recovery, fluorinated films are more adequate on one-way sensors.

1. INTRODUCTION

Plasma polymerization of hexamethyldisilazane (HMDS) is quite common on plasma science and attends to different research and technological purposes. Due to the high hydrophobic character [1] and good adhesion properties [2], HMDS plasma deposited films are useful on surface protection, textile, optical, medicine, etc [3-5]. On sensors development, due to the hydrophobic character and easiness of organic compounds adsorption, HMDS plasma polymerized films might be useful not only for surface protection [6] but also as sensitive layer as well [7]. However, to the best of our knowledge, up to now no attempt was made in using HMDS films for capacitive sensors development.

Nonetheless, HMDS polymerized thin films deposited on low frequency plasma reactor show important mechanical, electrical and optical properties [7]. HMDS films show good step coverage and their surfaces adsorb VOCs (volatile organic compounds) present either on gaseous or liquid solutions; furthermore, the refractive index is quite similar to the silicon oxide films.

Therefore, especially due to the ability to promote adhesion, HMDS films and even their composites with particles were deposited on microchromatographic columns and used to VOCs preconcentration in gaseous samples [8, 9] or liquid phase [10]. Current–voltage (CV) curves of silicon sample covered by HMDS film presented a quick, reversible and reproducible response for N2 saturated with 2-propanol vapor whereas a drop of n-hexane deposited on HMDS surface decreases the electrical current irreversibly, probably owing to film swelling [7]. Moreover, their refractive index favored the production of optical sensors, based on a Mach-Zehnder Interferometer, for VOCs detection [11].

The use of capacitive sensors presents some advantages due to the easiness of manufacturing and the simple architecture, which the commonest architecture composed of one dielectric contained by two parallel metal plates [12]. On such sensors, if the distance between the internal surfaces of the capacitor plates is smaller than the capacitor plates areas (Equation 1), a simple two-dimensional electrical field modeling can be applied, i.e., the sensor can be described by Eq. (1) [13]. Furthermore, the dielectric property is dependent on the amount of dipole momentum and its polarization, due to the existence of an electrical field. Therefore, the capacitive sensors can vary its capacitance if these dipoles are perturbed somehow, for instance by dipole reorientation owing to contaminant presence.

$$C - \frac{\varepsilon.S}{d}$$
 (1)

where: C = capacitance;

- d = distance between the internal surfaces of the capacitor plates;
- S = capacitor plates areas;
- ε = electrical permittivity of the medium.

Thus, the aim of this work was the electrical characterization of HMDS thin films and fluorinated composites aiming further application on capacitive sensors manufacturing. Whereas HMDS films are adsorbent but swell in presence of hydrocarbons [7], fluorinated compounds can protect the surface against aggressive environment [14].

2. EXPERIMENTAL

2.1. Concepts involved

In this work silicon was used as substrate (see experimental), the polymeric thin film acts as a dielectric material

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and the electrodes are positioned as external layers during measurement (Figure 1); therefore, the whole structure resembles a MOS capacitor.

Due to the existence of charges on the device, the correct model to explain the capacitance values on MOS capacitor three different interfaces: must consider elecsemiconductor/dielectric, trode/semiconductor. dielectric/electrode and three surface conditions: accumulated, depleted and inverted. The interaction of such parameters leads to a curve similar to the one shown in Figure 2, which also depicted the electrical model that interprets the observed behavior. On the accumulated region the measured capacitance is practically due to the polymeric material (dielectric, C_D) but on the other two regions, mainly owing to charges on the interfaces, another capacitance (C_s) and charge depletion occurs on silicon substrate, with maximum depth of the depleted region (W) obtained on the inverted condition [15].



Figure 1 - Schematics of experimental setup (A) and correlation with MOS capacitor (B).

2.2. Materials and methods

Silicon wafers were used as substrates because: 1) most sensors are silicon devices; 2) HMDS thin films show good adhesion to silicon surface; 3) the substrate is plane and the surface roughness is negligible, which help chemical and electrical characterization. Therefore, films were deposited on silicon wafers, type p, 100, 10–20 Ω cm, (Silicon Sence, Inc., USA) using HMDS (Fluka Chemie GmbH, Switzerland) and 2,3-dihydrodecafluoropentane (Vertrel®, Clarus Technology do Brazil, Ltda). Plasma was produced in homemade DC powered equipment described elsewhere [8]. Figure 3 shows plasma chamber schematics, which points out two injection systems and three electrodes (detail in Figure 3). The two injection systems are completely independent and can be powered; thus the principal injection system is the anode and the auxiliary injection system the auxiliary electrode. This auxiliary electrode is used to insert not only reactants but also particles inside the plasma region. Although auxiliary electrode might be powered, it was used only in floating condition during depositions and the sample was kept on the cathode. The plasma integrity near the substrate is achieved using two permanent magnets with 300 G on plasma region. The Knudsen number on such chamber is lower than 0.007 for all process conditions utilized.



Figure 2 - CV characteristic curve and the associated electrical model.

This equipment allows the production of composite and double layers material in a single step, i.e., without removal of the sample from the plasma environment. Double layer procedure aims the sequential production of two or more layers of plasma deposited films. Composite film corresponds to a mixture of two or more discontinuous films, in which granule dimension might vary from nanometric to milimetric range, or a film involving particles. On this work, it was produced and tested HMDS, fluorinated, double layers with fluorinated film on top and a composite of HMDS and fluorinated films.



Figure 3 - Plasma chamber schematics.

Plasma deposited films were characterized by infrared spectroscopy (FTIR, BioRad, USA) and Scanning Electron Microscopy (SEM, NovaNanoSEM 400, FEI, USA) to determine chemical structure and non-uniformities, respectively. For electrical characterization, film thickness was approximately 100 nm for all samples, deposited on 2 cm square silicon piece. Electrical characterization measured capacitance as a function of voltage in high frequency (1 MHz) and DC BIAS adjusted to obtain accumulation and inversion conditions, as stated in Figure 2; these values usually ranged from 0 to 30 V. Measurements used an impedance analyzer (Agilent 4294, USA) and the results used in this work are the average of three consecutive measurements. Adsorption measurements used 2-propanol and n-hexane as reactants and the procedure consisted in film exposure to airflow saturated with the reactant, with a flow rate of 5 sccm at room temperature, during 10s. Reactant removal was attempted by exposure to airflow at same conditions used during adsorption cycle. Long exposure times, approximately 1 minute, were also used in order to evaluate saturation of the film surface.

3. RESULTS AND DISCUSSION

The main chemical and physical characteristics of deposited films are explained and then the electrical measurements are evaluated.

3.1 Chemical and physical characteristics

Plasma films were obtained in conditions, as described in Table 1 that correspond to the highest deposition rate. HMDS and fluorinated compounds present different deposition mechanisms; whereas HMDS is an easily plasma polymerizable molecule, fluorinated reactants request high power to produce the deposition precursors. On the other hand, HMDS deposition is based on ion/molecule reactions but fluorinated chemistry depend on free radicals. Furthermore, HMDS activated species promptly adhere on silicon surface but not the fluorinated compounds [8,9,10]. Therefore, as can be seen on Table 1, HMDS deposition requires lower power and presents higher deposition rate. Moreover, in order to assure fluorinated deposition, double layer and composite samples must be produced on higher voltage and the fluorinated compound must be admitted near the surface, which favors adsorption on sample surface.

Table 1 - Deposition conditions on plasma chamber											
FILM	Reactant in the injection system		Deposition Pressure Range	Voltage during deposition range	Deposition rate						
	auxiliary	principal	(mTorr)	(V)	(A/min)						
HMDS	HMDS	HMDS	10 - 200	300 - 450	30 - 100						
Fluorinated	Fluorinated	Fluorinated	10 - 200	350 - 600	Very low						
Double layer	Fluorinated	HMDS	10 - 200	350 - 600	nd						
Composite	Fluorinated	HMDS	10 - 200	350 - 600	nd						

nd = not determined since there are more than one layer or compound involved

FTIR analysis points out the existence of HMDS and/or fluorinated films along with oxygenated species, as previously reported [8], and Table 2 shows the FTIR relative intensities to intense bands on these films. HMDS thin films present bands at 2950 cm⁻¹ (CH stretching), 1730 cm⁻¹ (oxygenated species), 1450 cm⁻¹ (CH₂), 1370 cm⁻¹ (CH₃), 1260 cm⁻¹ (Si(CH₃)₃ rocking), 1180 cm⁻¹ (Si–N bending), 1070 cm⁻¹ (Si–O) [16]. Bands of fluorinated films are located at

3300 cm⁻¹ (CH stretching and/or CF surrounded by oxygen), 2950 cm⁻¹ (C–H stretching), 1300 cm⁻¹ – 1000 cm⁻¹ (CF stretching) [17-20].

HMDS deposition is mostly based on ion/molecule reaction [8], which requires bombardment to achieve high deposition rate. Consequently, variation on deposition parameters leads mainly to differences on topography [21]. On the other hand, fluorinated films are obtained with free radicals [22],

which means that adsorption on silicon surface is an important driving force and the resultant film surface is smooth [10].

 Table 2 - FTIR relative intensities to HMDS and fluorinated

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HMDS film (%)										
Normalized	2950	1730	1450	1370	1180	1070				
to 1260	cm^{-1}	<i>cm</i> ⁻¹	<i>cm</i> ⁻¹	cm^{-1}	cm^{-1}	cm^{-1}				
cm ⁻¹	0.09	90.7	36.7	21.2	60.5	48.8				
Fluorinated film (%)										
Normalized	3300	2950 cm ⁻¹		1300	1260 cm ⁻¹					
to 1068	<i>cm</i> ⁻¹			<i>cm</i> ⁻¹						
cm ⁻¹	87.5	21.1		25.1	35.5					

Samples obtained with distinct deposition parameters were analyzed by SEM and Table 3 shows typical results. The main difference between samples 1 and 2/3/4 was the sample position; whereas samples no. 2/3/4 were maintained on the electrode, sample 1 was placed vertically; therefore, the topographic differences on that samples were mainly due to ion bombardment influence. Sample 1 is smooth and its appearance is similar to the thin gold layer deposited on top of it. The clusters seen on samples 2/3/4 are characteristic in HMDS deposition and they are the result of simultaneous adhesion and bombardment inducing surface reactions. On these samples, voltage variation will influence cluster dimension; therefore samples 3/4 are used to evaluate reproducibility if cluster dimensions decrease. Fluorinated sample (no. 7) is similar to sample 1 due to the deposition mechanism, based mainly on free radicals. Double layer deposition (sample no. 5) shows big clusters due to adhesion of activated species, probably free radicals, to the previously deposited HMDS thin film surface; nonetheless, the sample is not so rough as sample 2, which indicates that planarization effects took place. Composite samples (no. 6) show nonuniformities with each cluster presenting mostly HMDS or fluorinated film. Thus, the comparison between samples 5 and 6 electrical characteristics will provide insights on the importance to the existence of a fluorinated layer, continuous or non-continuous respectively, on the surface.

3.2. Electrical characteristic

3.2.1. Non-polar reactant

Non-polar reactants, such as n-hexane, are easily adsorbed on HMDS thin film surface but also cause film swelling. Figure 4 shows CV curves to samples 1 to 4, as deposited, exposed to air saturated with n-hexane vapors and after that, in one attempt of reactant removal, exposition to air during 1 minute. The voltage range showed in the graphs was chosen to depict the interval with maximum variation and the curves correspond to an average of three consecutives measurements; furthermore, none of these samples showed hysteresis before exposure to n-hexane.

All samples before exposure showed similar curves with inversion condition up to 2-3V and maximum capacitance value from 100 pF to 200 pF, which seems to indicate that thickness is the main parameter, not topography. These capacitance values are also promising considering the dimensions of the sensitive layer; just for comparison, [23] capacitive sensors manufactured using glass slides and thick films (larger area and thickness) produced capacitance values of 1nF. Moreover, the total capacitance changed at least 20%, i.e. minimum sensor response of 0.2, which is similar to the obtained values on interdigitated capacitive sensor arrays covered by methacrylic polymer at detection of 5000 ppm H_2O [24]. However, the same setup shows a sensor response of 0.00525 on the presence of 5000 ppm ethyl acetate. Furthermore, in a 10s exposure, for n-hexane the total sample amount that could reach the film is approximately 2 umol/cm²; thus, electrical measurements show a good result if compared to quartz crystal measurements (QCM), since on such technique the detection limit is the injection of 200 $\mu g (3.6 \ \mu mol/cm^2) [8].$

After exposure to n-hexane vapors there is a consistent dislocation on the inversion condition range, probably due to the viscoelastic behavior of these films that changes the distance among permanent dipoles, which function as charge changes inside a capacitor. These dipoles, for instance due to Si-O bonds, are probably also responsible for changes on the other two conditions. Moreover, the overall capacitance lowers, probably due to the diminishing on the effective thickness of the dielectric (polymeric material), caused by adsorption. However, correlation between dipoles changes, adsorption layer formation and the electrical response is not straightforward, i.e., depends on several parameters and the resultant variation can be distinct from one sample to the other. Nonetheless, the inability to return the signal to the former values even after one-minute exposure to noncontaminated air is a good indicative that film swelling is irreversible on such case. Fluorinated film is not sensitive to n-hexane exposure but can permeate reactants, as explained later.

3.2.2. Polar reactant

Figure 5 shows typical results obtained by film exposure to 2-propanol vapors. On HMDS films (Figure 5a), the maximum capacitance clearly changed due to exposure and a partial recovery is easily obtained using airflow. This condition is probably due to adsorption layer formation that diminishes dielectric thickness on the capacitor, but, differently than n-hexane exposure, there is no distortion on other conditions, i.e., corresponds to a reversible system situation. In a 10s exposure, the total sample amount that could reach the film is 0.4 μ mol/cm2 for 2-propanol, but even on such detection range the sensor response is high (0.3); on the other hand, the minimum injection required on QCM measurements is much bigger, 300 μ g (8 μ mol/cm²) [8].

Fluorinated film (Figure 5b) has low sensitivity, with no signal variation in 10s exposure and just a small change ob-

tained in the maximum capacitance after one-minute exposure. Moreover, only exposure for more than 15 minutes leads to variation on maximum capacitance similar to the one obtained with HMDS, but this change is quickly lost in the airflow.



Table 3 - Typical results for SEM analysis of HMDS and fluorinated films (deposition pressure = 100 mTorr).

Fluorinated film Reactant in the injections systems (principal and auxiliary): Vertrel® Sample no./voltage during deposition: 7/ 440 V





Sample nro. 4

Figure 4 - CV curves to samples 1 to 4 before and after exposure to n-hexane vapor.

Double layers (Figure 5c) also show a sensor response of 0.3 but with a permanent change on CV curve due to reactant retention on the interface between fluorinated and HMDS films. This change occurs because 2-propanol can permeate through the fluorinated film [8], which also avoids reactant removal by airflow exposure and the signal does not change after several minutes exposure to clean air. Furthermore, electrical measurements show better detection limit if compared with QCM measurements, which is 300 µg.

Composite films (Figure 5d) show behavior similar to the HMDS samples, owing to the high amount of HMDS films on the surface. Nonetheless, the partial signal recovery indicates that film swelling is probably limited by the presence of the fluorinated clusters on the surface.

A sensor response to µmol indicates these films to ppm range detection. This result is coherent with measurements obtained [11] on a Mach-Zehnder Interferometer; however, capacitive sensors are much more easily implemented. Furthermore, in all measurements, before reactant exposure, the curve is reproducible with variation on maximum capacitance lower than 1pF; however, this behavior changed after exposure, which indicates these films as qualitative sensors. Nonetheless, changes on CV curve could be useful if the reactant concentration determination is not relevant but presence detection is; on such situation, only the change must be sensed and a much lower value would be achieved, typically on the sub-ppm range





Figure 5 - CV curves to films exposed to 2-propanol vapor: (A) HMDS, fluorinated (B) double layer (fluorinated on top) (C) or composite (D) films.

4. CONCLUSIONS

This work evaluated the capacitive response of HMDS and fluorinated thin films and pointed out that HMDS and fluorinated thin films are promising on sensors development. Nonetheless, whereas HMDS films seem to be useful on any capacitive sensors device; due to the difficulty in signal recovery, fluorinated films are more adequate on one-way sensors. Both films are adequate to qualitative sensors and can be used at least on ppm range.

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