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# Elaboration and Characterization of Thin Water Molecule Sensitive Layers Deposited from Hexamethyldisiloxane

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# Elaboration and Characterization of Thin Water Molecule Sensitive Layers Deposited from Hexamethyldisiloxane

**Noubeil Guermat**

## Abstract

This paper reports the study of the electrical properties of plasma polymerization of hexamethyldisiloxane (pp-HMDSO) thin film based sensors. Thin water molecule sensitive layers were deposited from a hexaméthyldisiloxane precursor on a tow-interdigited electrode at low frequency power (19 KHz) plasma conditions. The sensor was calibrated in terms of impedance as a function of relative humidity, using a Frequency Response Analyzer. The electrical properties of the sensor are measured. The deposited film sensor exhibited an accepted sensitivity (impedance change from $10^6$ to $10^4$ Ω in the humidity range of 30–95% RH), fast response (8 and 34 s for adsorption and desorption between 35% RH and 95% RH, respectively), and the current intensity increased from $10^{-10}$ to $10^{-6}$ A in the explored range of RH (25-95% RH). The change in the current of pp-HMDSO with respect to increasing and decreasing RH (hysteresis) of no more than 3% has been observed. The structural analysis of the sensitive layer was carried out by theFourier Transform Infrared spectroscopy (FTIR). The films showed good sensitivity to the water molecule due to the presence of hydroxyl groups OH. These groupments provide the adsorption sites for water and play an important role in the humidity sensor properties, make the HMDSO films showed promising characteristics for humidity sensor development.

**Keywords:** Electrical characterization, Hexamethyldisiloxane, Humidity sensors, Thin film.

## Introduction

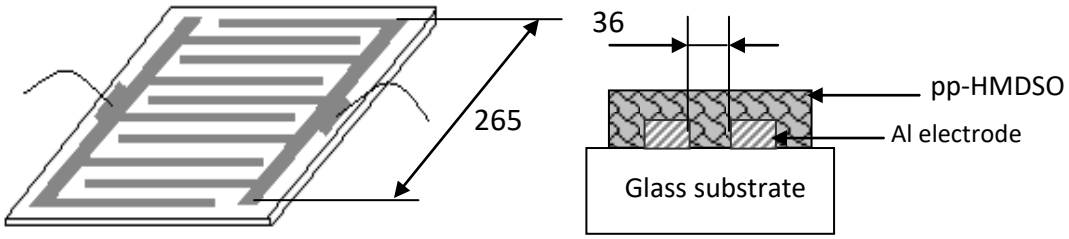
Humidity sensors are widely used in the surveillance and control of industrial processes, domestic and environmental applications. There is a growing interest in developing low cost sensors capable to generate high sensitivity, short response time, good reversibility and high temperature resistance [1]. Organic silicon compounds are used in a large range of applications like thin film deposition by plasma polymerization. The use of plasma polymerized films as an insulating and coating for microelectronic devices are widely appreciated [2, 3], however, they are not commonly used for the fabrication of absorbing layers. In order for the film to be useful as sensitive layers, it must be homogenous, free of pinholes even at low fabrication costs, high thermal and chemical stability and good adhere to various substrates. Films elaborated in a glow discharge can fulfill all these requirements. Plasma polymerized layer of hexamethyldisiloxane (HMDSO) has been shown to be able to absorb water vapor [4-6]. The ability of these layers to absorb water molecules gave rise to investigate the humidity sensing. In this paper, in order to learn more about the efficacy of plasma polymerization as a technique for the deposition of water moisture sensitive layers, we used plasma polymerization to deposit HMDSO thin films on two intredigitated aluminum electrodes evaporated on the glass substrate. The study presents the results for structural and electrical sensing properties of the elaborated sensitive layers.

## Experiments

### *Film Deposition*

The device concept consists of a resistive-type sensor composed of thin water molecules sensitive layer (HMDSO) deposited on a clean glass substrate with com-shape aluminum electrodes (interdigitated structure IDS). Figure 1 represents the top view and the cross section of the sensor. The Al electrodes with spaces of 63 μm between the tracks were evaporated on clean glass substrates.

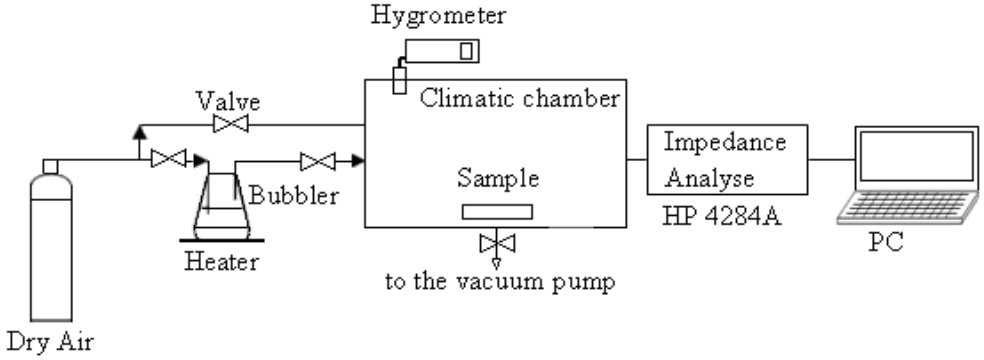
**Figure 1.** *Schematic Top View and Cross Section of the Sensor Design*



The polymerization took place in a glow discharge at 19 kHz in a homemade coactively coupled parallel plate reactor. The schematic view of the plasma reactor used for HMDSO thin layers deposition is shown in Figure 2. The system consisted of a bell-jar chamber (310 mm in diameter, 250 mm high) with two parallel electrodes separated by a 2.5 cm, vacuum system (composed of Alcatel primary pump) and a monomer inlet system. The pressure in the reactor was monitored by a pressure measurement system (Pirani jauge). On the lower electrode, the substrate was horizontally placed and the reaction chamber was evacuated down to $10^{-2}$ mbar. The HMDSO flow rate was kept constant for all the deposition process. The power during the polymerization was controlled by a 19 kHz generator. During deposition the discharge power and the pressure were fixed to 8 W and 0.4 mbar, respectively. The film thickness was measured using a Tencor profilometer and a microspot beam spectroscopic ellipsometer (Sopra GES5) with an incident angle of 75.6° (silicon Brewster angle).

*Films Characterizations*

**Figure 2.** *Schematic View of the Plasma Reactor*



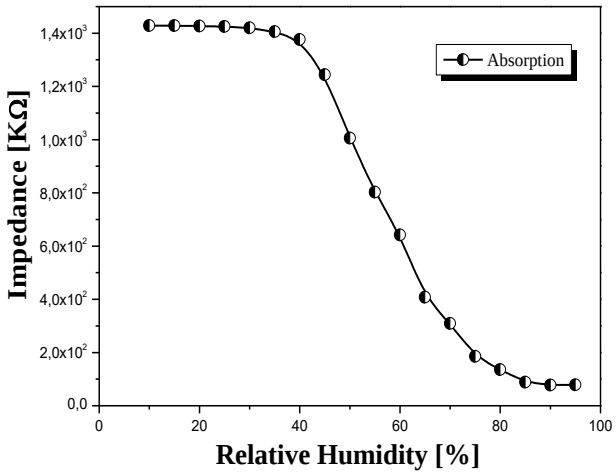

Humidity response behavior of the sensors at a different humidity range was investigated in a humidity chamber system. A temperature and humidity sensor (commercial Testo 610 model with the resolution of ±0.1%) was used to monitor the relative humidity (RH) and to measure temperature stability in the climatic chamber. Relative humidity was varied from 10 to 95%. The electrical sensing properties were carried out by two methods: the current response of HMDSO films-based humidity sensors were measured with a 6512 Kheithly digital electrometer and impedance values of sensors in different humidities were recorded using HP impedance analyzer (4284 LCZ meter). The chemical analysis of the plasma-polymerized HMDSO films was performed in the range 400-4000 $cm^{-1}$ using a Nicolet Avatar 360 FTIR spectrometer.

## Experimental Results

*Electrical Sensing Properties*

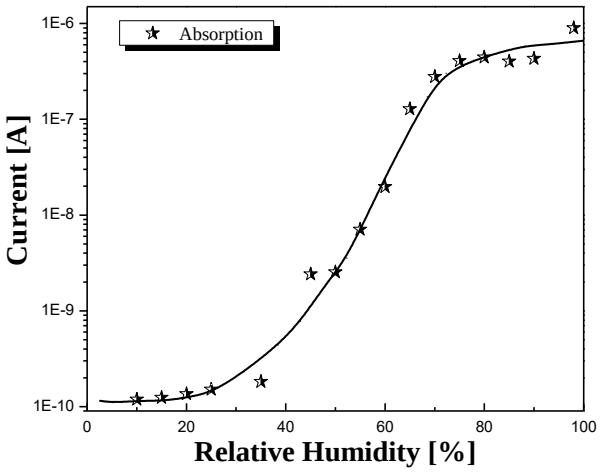
The plasma polymerized HMDSO thin films deposited on two-intredigitated aluminum electrodes, they were used as sensor element and evaluated for humidity detection under an alternative signal with amplitude of 5V and frequency of 1 kHz has applied. Figure 3 shows the variation of the impedance response with relative humidity (between 10 to 95%) for pp-HMDSO film at temperature of approximatively 27 °C. For low RH (from 10 to 30 %) ranges, the deposited films were found to be insensitive to air moisture.

**Figure 3.** *Typical Impedance Response of PPHMDSO-based Humidity Sensor*



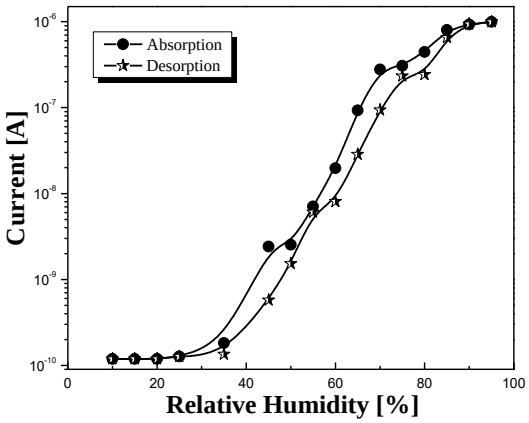

The pp-HMDSO film sensor did not show a visible change of the electrical impedance, the value of this later was in order of about $10^6$ Ω. However for high RH (from 40 to 95%) ranges, the electrical impedance decreased significantly until reaching the value of $10^4$ Ω. This behavior has also been observed for silica aerogel thin films based humidity sensor [7]. The interpretation of the electrical response is based on diffusion process of water in the vapor phase inside the porous material. Electromecanical dissociation of water occurs upon applying a voltage leading to the formation of OH groups. These later are able to promote the hopping of $H_3O^+$ from one site to another; consequently a partial ionic conduction can be achieved from the dissociation of hydrogen protons [8].

**Figure 4.** *Current Response of pp-HMDSO-based Humidity Sensor*



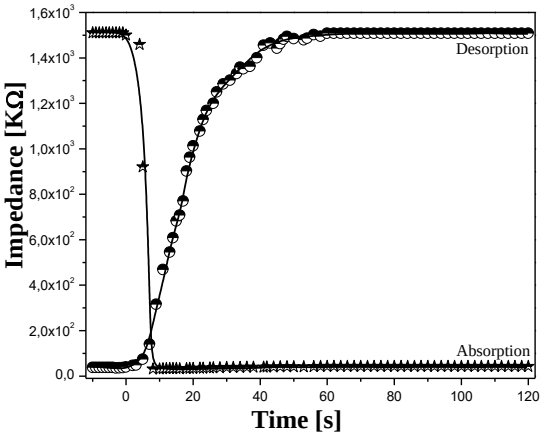

In Figure 4 the current responses of pp-HMDSO-based sensor towards RH variations are reported in absorption and desorption mode. In the low RH range, the current response did not show a visible change. This behavior may be attributed to a low proportion of protons to be transferred to adjacent water molecules for inducing electrical conduction [8]. However, for high relative humidity range (25-95%) a sharp increase of the current intensity has been observed. The current intensity of the sensor changes form $10^{-10}$ to $10^{-6}$ A in the explored range of RH. These results indicated that pp-HMDSO-based sensors exhibits better humidity sensing characteristics in comparison with ones based on poly(monosubstituted)acelylene [8] and poly(p-diethynylbenzene) [9]. Furthermore, pp-HMDSO-based sensor showed small hysteresis not more than 3% (Figure 5), which indicated that the reversible absoption/desorption will be easily achieved.

**Figure 5.** *Humidity–current Characteristics of pp-HMDSO Based Sensor*



Another important issue regarding the sensing properties is the response time. The variation in impedance of pp-HMDSO with time when RH was changed between these two extremes (35 and 95% RH). The response time, defined as the time needed to reach 90% of the total impedance change for a given relative humidity, and recovery time defined as the time taken for the signal to come to within 10% of the initial value. In Figure 6, we report the dynamic impedance response versus time at different humidity steps for a typical device. It is found that the sensor exhibits a fast response and recovery time, the response and recovery times were in the order of 8 s and 34 s, respectively, which are among the best results reported for resistive type humidity sensor [10, 11]. The faster response time to humidity of pp-HMDSO sensor might be due to regular morphology and suitable thickness of the sensing layer. Films deposited by low frequency plasma from pure HMDSO have been reported to be homogeneous, without pinholes and defects [6]. This is convenient for efficient absorbing and desorbing of water molecules. The response time associated with the absorption process is shorter than that associated with the desorption process. This asymmetry in diffusion of water inside the polymer film is a characteristic property of most humidity sensors, where kinetics of desorption of water molecules from the pores are slower than their absorption [10].

**Figure 6.** *Response-recovery Properties of pp- HMDSO Sensor*



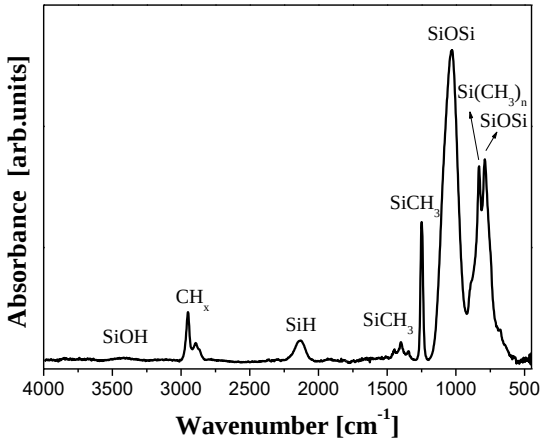

*Structural Properties*

FTIR measurements were carried out in order to investigate the chemical structures of deposited layers (Figure 7). The main bands peaks observed in this spectra is summarized in Table 1.

**Table 1.** *Characteristic Infrared Absorption Bands of Organic Compounds*

| **Wavenumber [$cm^{-1}$]** | **Group** |
|---|---|
| 800 | $Si-(CH_3)_2$ |
| 840 | $Si-(CH_3)_3$ |
| 1049 | Si-O-Si |
| 1261 | $Si-CH_3$ |
| 1410 | $Si-CH_3$ |
| 2146 | Si-H |
| 2902 | $CH_2$ |
| 2967 | $CH_3$ |
| 3669 | Si-OH |

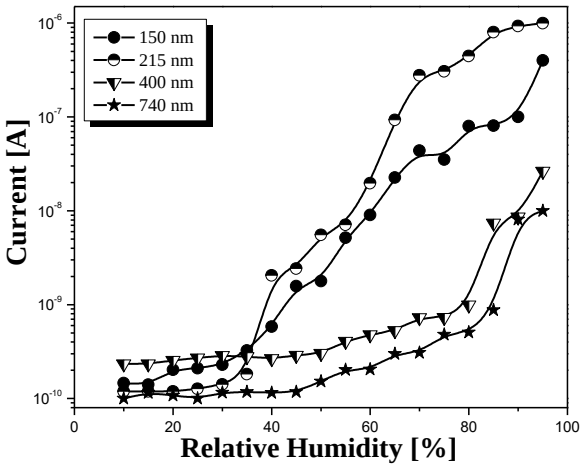
**Figure 7.** *Typical FTIR Absorption Spectrum of pp-HMDSO Film*




FTIR absorption spectra of pp-HMDSO film deposited at 8 W reveals strong peaks at around 800, 840 and 1049 $cm^{-1}$, which, correspond respectively to $Si-(CH_3)_2$, $Si-(CH_3)_3$ and Si-O-Si groups. Another peak which is representative of the organic groups ($Si-CH_3$) appears at 1261$cm^{-1}$. The sensitivity to humidity is highly affected by the presence of the organic groups ($Si-CH_3$). The sensor properties can be improved by improving the wettability of the sensitive layer by incorporating oxygen, which can increase the polar oxygen species and reduce the methyl groups. However, FTIR spectrum shows also a peak with low intensity at around 3660 $cm^{-1}$ attributed to the stretching mode of surface silanols (Si-OH), which can contrary provide the hydrophilic capability for water absorption through a hydrogen-bonding force.

*Effect of pp-HMDSO Film Thickness on the Electrical Sensing Properties*

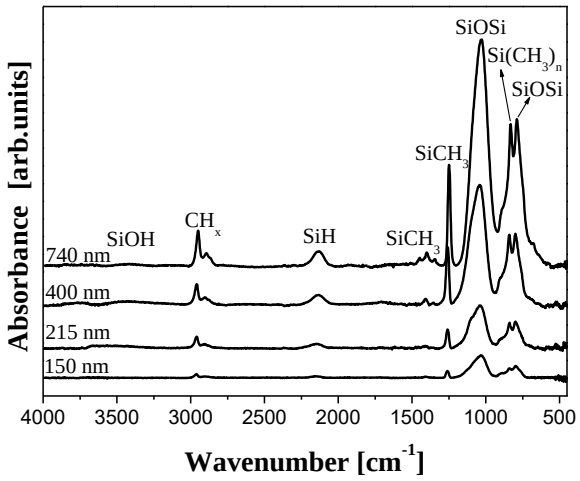
**Figure 8.** *Current Response of pp-HMDSO Humidity Sensor with Different Thickness*




Since the interpretation of the electrical response is based on the diffusion process of water in the vapor phase inside the sensing layer pores, the effect of the deposited film thickness on the electrical sensing properties has been investigated. During the plasma deposition process, both the discharge power and the monomer partial pressure were fixed to 8 W and 0.4 mbar respectively. The discharge time was varied in order to elaborate sensors with different layer thickness. The typical electrical response of humidity sensor based pp-HMDSO is plotted in Figure 8 for different film thickness.

Figure 8 shows the evolution of the current response of pp-HMDSO based sensor with the variation of the sensitive layer thickness. It was shown that the current of the sensor increases from $10^{-10}$ A to $10^{-6}$ A in the range of 10 to 95% RH for low layer thickness sensor and from $10^{-10}$ A to $10^{-7}$ A for high layer thickness sensor. Current response evolution with pp-HMDSO film thickness variation showed that the sensitive capability of the plasma deposited layer to humidity was significantly reduced by the increase in film thickness. This behavior may be explained by the fact that as the deposited layer thickness increases the film becomes denser. The film densification leads to a reduction in the size and also in the number of the film pores, by consequent the diffusion process of water in the vapor phase inside the sensing layer pores can be significantly reduced leading to the reduction of the ionic conduction.

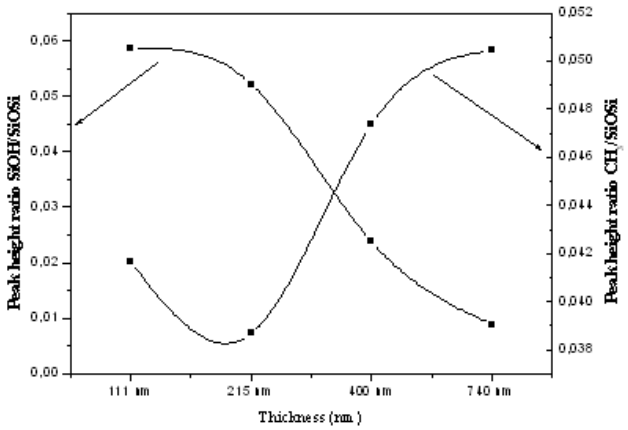
**Figure 9.** *FTIR Spectra of Thickness Varied pp-HMDSO*




In order to elucidate the decrease of the senility with the increase of the film thickness, FTIR analyses were carried out in transmission mode for four plasma polymerization processes. The resulting spectra of the deposited layers achieved from pure HMDSO at 8 W are displayed in Figure 9. The spectra revealed strong peaks of the methyl groups at 838 $cm^{-1}$ due to Si-$(CH_3)_3$ vibration. This organic group makes the film more water repellent and increases the films surface hydrophoby. However, it contains a low amount of surface hydroxyl (Si-OH) groups at around 3660 $cm^{-1}$, which can contrary provide hydrophilic capability for water absorption through a hydrogen-bonding force.

Figure 10 shows that ratio of $CH_3$ at around 838 $cm^{-1}$ and the main peak Si-O-Si increases with the increasing discharge time. Furthermore, the ratio of Si-OH groups at around 3660 $cm^{-1}$and the main peak Si-O-Si decreases with increasing film thickness. This difference in chemical structure may be explained by the fact that increasing discharge time enhance the formation of the methyl radicals ($CH_3$) and the hydroxyl groups (Si-OH) may be replaced by Si-H and probably by Si-Si bonding [12]. The replacement of the hydroxyl groups by Si-H or Si-Si leads to the film densification, which decreases significantly the absorption of the water vapor and by consequence the sensitivity of the deposited layer to humidity [12].

**Figure 10.** *Variation of the Peak Height Ratio of Methyl and Hydroxyl Absorption Bands with Discharge Time*




## Conclusions

The humidity sensor based on pp-HMDSO thin film exhibited a accepted sensitivity (current change from $10^{-10}$ to $10^{-6}$ A in the humidity range of 10-95% RH), shorter response–recovery time with small hysteresis. Electrical sensing properties showed that the sensitive capability of the plasma deposited layer to humidity was significantly reduced by the increase in film thickness. The FTIR analysis revealed that the increasing discharge power enhances the formation of methyl groups and replaces the hydroxyl bonding Si-OH by Si-H or Si-Si leading to film densification. The presented preliminary electrical characterization results showed the viability of using plasma polymerization of HMDSO for humidity sensors development but more detailed electrical characterization need to be carefully done in the future work. The humidity sensing of the film can be improved by incorporating oxygen in order to reduce the proportion of methyl groups and increase the proportion of polar groups.

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