

CHARACTERIZATION OF PLASMA POLYMERIZED THIN FILMS DEPOSITED FROM HEXAMETHYLDISILOXANE USING (PECVD) METHOD

Hisham M. Abourayana, Nuri A. Zreiba, Abdulkader M. Elamin⁽¹⁾

Materials and Metallurgical Engineering Department, Al Fateh University, Tripoli - Libya

⁽¹⁾National Bureau for Research and Development, Plasma Research Laboratory, Tripoli - Libya

الملخص

في هذا العمل تم ترسيب فيلم من البوليمر على عينات من الزجاج وسبيكة من الألومنيوم نوع (6061) بطريقة الترسيب بالتبخير الكيميائي المدعم بالبلازما عند درجة حرارة الغرفة وبقدرة متغيرة لمولد موجات الراديو المستخدم في توليد البلازما باستخدام الهيكساميثيل داي سيلوكسان كمادة بادئة. الخواص السطحية للفيلم المترسب تمت دراستها بقياس زاوية التلامس (θ) وباستخدام المجهر الإلكتروني الماسح. أظهرت النتائج زيادة زاوية التلامس وكذلك نعومة السطح بزيادة قدرة مولد موجات الراديو. البنية الكيميائية للفيلم المترسب تم تحليلها باستخدام جهاز التحليل الطيفي للأشعة تحت الحمراء الممتصة والمنعكسة بنظام تحويل فوريير للأشعة تحت الحمراء وأظهرت النتائج زيادة تركيز الهيدروجين وقلّة تركيز الأكسجين مع زيادة قدرة مولد موجات الراديو. قابلية الفيلم لحماية سبيكة الألومنيوم نوع 6061 من التآكل تم إختبارها بمنحنى الجهد الديناميكي في محلول كلوريد الصوديوم بتركيز وزني 3.5%، حيث أظهرت النتائج أن كفاءة الفيلم للحماية من التآكل تزداد بزيادة قدرة موجات الراديو.

ABSTRACT

Organic polymer thin films have been deposited on glass and aluminum alloy type 6061 substrates at room temperature and different radio frequency (r.f.) powers by plasma enhanced chemical vapor deposition (PECVD) method, using hexamethyldisiloxane (HMDSO) as organic precursor. Surface properties were characterized by scanning electron microscopy (SEM) and contact angle measurements. The SEM images indicate that the surface roughness decrease with increasing r.f. power, and the results of contact angle measurements indicated that the films deposited at the r.f. power 50 and 100 watt is hydrophilic while the one prepared at 150 watt is slightly hydrophobic ($\theta > 90^\circ$). On the other hand, chemical properties were characterized by means of fourier transformed infrared spectroscopy (FTIR). The results indicated that, with the increase of r.f. power, the concentration of hydrogen in the film increases, while the concentration of oxygen decreases. The corrosion protective abilities of films deposited on aluminum alloy type 6061 as a substrate were examined by potentiodynamic polarization measurements in 3.5 wt. % NaCl solutions. The

experimental results show that HMDSO films provided increased corrosion protective abilities with the increase of r.f. power.

KEYWORDS: Plasma; Polymerization; Precursor; Contact angle; PECVD; Film roughness; Transmittance; Protective efficiency

INTRODUCTION

Plasma polymerization is a process where the activation of organic vapors and gases in low temperature plasma (glow discharge) leads to the formation of polymeric materials. In the chemical sense, plasma polymerization is different from conventional polymerization reactions. In plasma polymerization, monomer and gas molecules are fragmented and ionized in plasma producing excited species, free radicals and ions. Adsorbed activated fragments recombine forming the plasma polymer. This type of synthesis has an atomic character in contrast to conventional radical and condensation polymerizations. In many cases, plasma polymers show distinguished chemical composition, structure, and chemical and physical properties from those formed by conventional polymerizations using the same monomer [1].

Plasma polymerization is gaining importance for last several years as a tool to modify material surfaces. Organic vapors can be polymerized at low temperatures using plasma enhancement. Plasma polymerization can also be used to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions because such processes involve electron impact dissociation and ionization for chemical reactions [2]. Plasma treatment is currently used in surface and interface engineering for improving adhesion, hydrophobicity, hydrophilicity, printability, corrosion resistance, selectivity, or for surface etching or cleaning. The main principle of the plasma technique is that the ionized and excited molecular radicals created by the electrical field bombard and react on the surface of the substrate. These ions and radicals may etch, sputter, or deposit on the substrate surface. As a result, the surface properties of substrates are modified. The plasma technique is a room temperature and environmentally benign process. Due to these characteristics, the plasma technique can be used for surface modification and thin film deposition on almost all substrates, including metal and alloy plates, polymer films, paper, glass, porous materials, and particulate matter [3].

Organosilicone films prepared by plasma polymerization provide good optical and mechanical properties. Most used monomers in this family of compounds include tetramethylsilane, vinyltrimethylsilane, HMDSO and hexamethyldisilazane containing Si, H, C, O or N atoms [2]. HMDSO is a choice of industries because it is a non-toxic material and no harmful materials are produced during processing. It can be used in production environment without any special safety considerations. Basic research studies on plasma polymerized organosilicones are reviewed by various authors. The films were found to be amorphous and pinholes free [2].

The use of plasmas for thin film coating deposition has been widely researched. The deposition of coatings for the purpose of corrosion protection has received some attention, which until recently principally focused on steel surfaces [4], although the protection of nonferrous metals has also been studied with copper [5,6] and aluminum [7]. One of the main advantages of plasma is the complete enclosure of the process, within a vacuum chamber, enabling the ready disposal of the process gases. Scale up from the laboratory is often considered an issue but the plasma equipment market is

mature and plasma equipment manufacturers can meet the demands of deposition at the industrial scale [7].

In this study, we report our results on the growth of plasma-polymerized organic thin films on glass and commercially aluminum alloy type 6061 substrates at room temperature using hexamethyldisiloxane precursors by PECVD method. The body of this paper will focus on performing analysis of physical and surface properties of plasma-polymerized organic thin films.

EXPERIMENTAL WORK

The experimental setup employed in this work, schematically depicted in Figure (1), is a multi-purpose system which enables thin film deposition, surface cleaning and treatment by plasma processes. Essentially, it is composed by a stainless steel cylindrical vessel, fitted with two circular parallel plate electrodes. A radiofrequency (13.56 MHz, 0-300 W) power supply is connected to the upper electrode via an impedance matching circuit. The system is evacuated by a rotary pump from atmospheric pressure down to 10^{-3} torr and then by a turbo molecular pumps. Base pressure reaches 10^{-5} torr which is low enough to provide good quality depositions. The admission of gases to the chamber is controlled by needles valves. HMDSO as a liquid compound is placed in stainless steel evaporation cells. These are coupled to the plasma reactor flanges using needles valves.

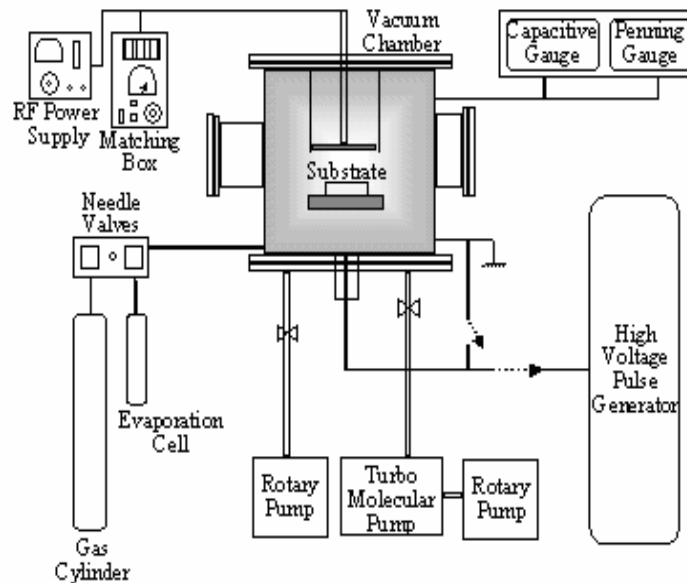


Figure 1: Experimental apparatus employed for film deposition.

The chamber pressure is monitored by a wide-range manometer, composed by a Pirani and a Penning gauges. For the plasma polymerization process, substrates are mounted in the lower grounded electrode. Glow discharge is generated by the application of radiofrequency power to the upper electrode while the chamber walls are earthed. Polymer-like thin films were deposited on glass and disk-shaped aluminum alloy type 6061 substrates by the plasma-enhanced chemical vapor deposition (PECVD). After cleaning the sample ultrasonically using acetone, isopropanol and

distilled water, the substrates were in situ pre-treated with Ar plasma to give an oxygen-free surface and a buffer layer for enhancing film adhesion. The general deposition pressure was 6×10^{-2} torr and the deposition time was 90 min. The deposition process was carried out at three different r.f. power levels of 50, 100, and 150 watt of r.f. power, HMDSO monomer was used as an organic precursor.

The chemical structure and surface properties of the plasma polymerized thin films deposited on glass substrates were analyzed with FTIR and contact angle measurements. Surface roughness of deposited films was investigated using scanning electron microscopy (SEM). The corrosion resistance of the 6061 Al-base alloy substrates both bare and covered by means of PECVD was carried out by potentiodynamic polarization measurements in standard 3.5 wt. % NaCl solution at room temperature.

RESULTS AND DISCUSSION

Chemical Structure

Figures (2a-2c) show the infrared spectra of the films deposited from HMDSO plasmas with various r.f. powers. Absorption bands related to the HMDSO film detected in these spectra are listed in Table (1) [8-10].

The FTIR spectra show a growth of the bands due to Si-CH₃ and CH₃ groups and a decrease of the bands due to Si-O-Si and SiOH groups when the applied power increases. The presence of Si-H groups is revealed by the weak absorption at 2127 cm⁻¹. This band is present only in the spectrum of the higher power (150 watt) prepared film. They indicate that the concentration of H is increased with r.f. power and the concentration of oxygen was decreased when increasing r.f. power.

Table 1 Absorption bands of HMDSO films detected in the spectra of Figures (4a-4c) [8-10]

Wavelength (cm ⁻¹)	Vibrational Groups
750 – 780	Bending (Si-O) in Si-O-Si
800 – 900	Rocking (CH ₃) in (Si-CH ₃) _x
1000 – 1050	Stretching asymmetric (Si-O) in Si-O-Si
1250 – 1280	Bending symmetric (CH ₃) in Si-(CH ₃) _x
1350 – 1410	Bending asymmetric (CH ₃) in Si-(CH ₃) _x
2100 – 2150	Stretching Si-H in Si-H _x
2900 – 2960	Stretching asymmetric CH in CH ₃
3250 – 3415	Stretching O-H in SiOH

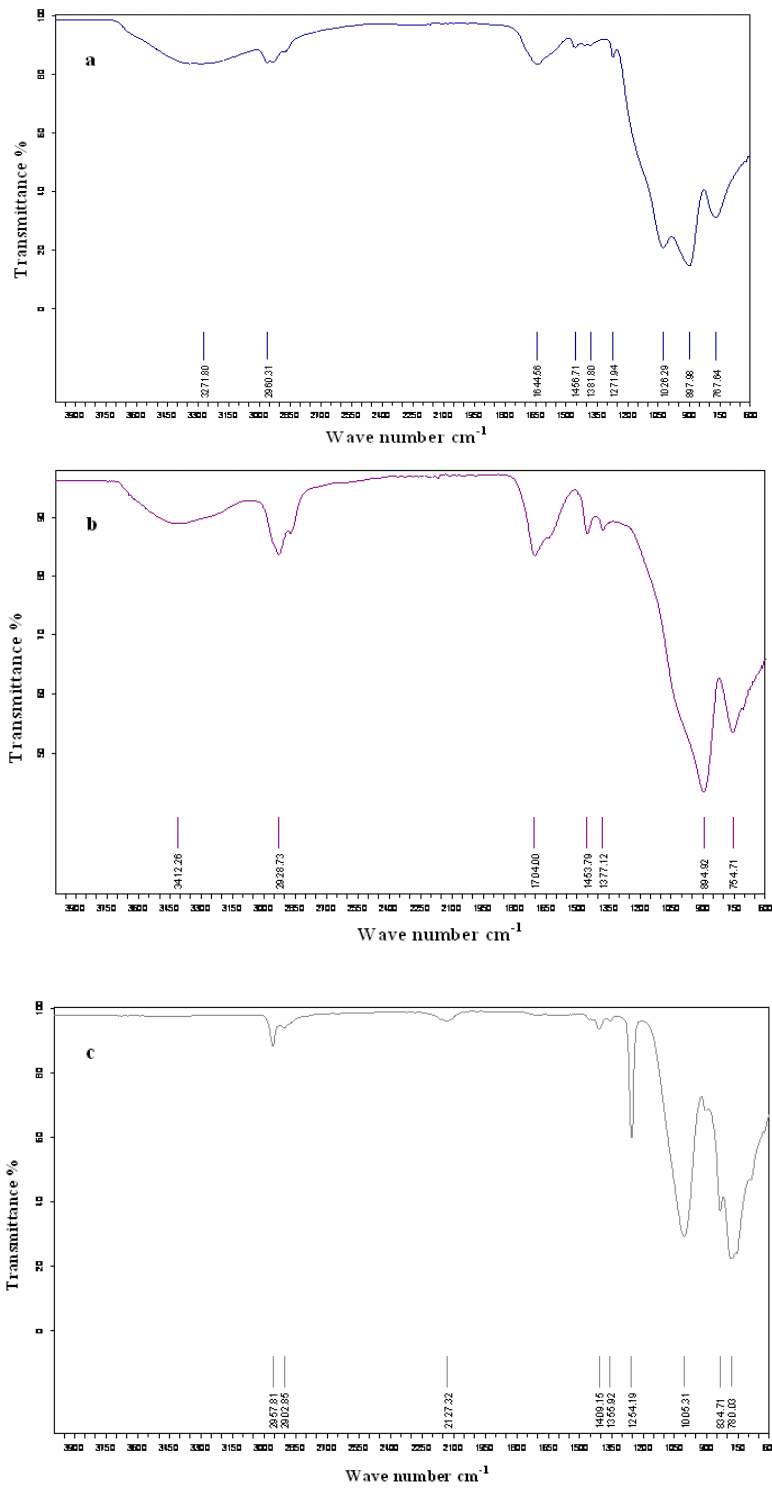


Figure 2: Infrared spectra of hexamethyldisiloxane films prepared with (a) 50 watt, (b) 100 watt and (c) 150 watt r.f. power

CONTACT ANGLE

Table (2) introduces the measured values the contact angles (θ) of the films deposited at 50, 100, and 150 watt r.f. power. The films deposited at 50 and 100 watt are hydrophilic, while the one prepared at 150 watt is slightly hydrophobic ($\theta > 90^\circ$). This result is consistent with the conclusion on the decrease of the oxygen groups present in the films with increasing the r.f. power, based on the infrared spectra of Figure (2a-2c). The interpretation proposed of a higher concentration of oxygen groups as the deposition is performed at 50 and 100 watt is corroborated by the lower contact angle of these samples.

Table 2: Contact angle of hexamethyldisiloxane films as a function of the r.f. power

r.f. power (watt)	Contact angle ($^\circ$)	Surface energy (dyne cm)		
		Polar	Dispersive	Total
50	51.0 ± 2.5	21.20	44.87	66.07
100	75.1 ± 1.6	11.75	34.21	45.96
150	97.6 ± 2.0	5.01	23.09	28.10

POTENTIODYNAMIC MEASUREMENTS

Figure (3) shows the potentiodynamic polarization curves for 6061 Al-base alloy substrates, both bare and covered with hexamethyldisiloxane films, deposited at various r.f. power levels. The corrosion potential shifts to more positive values as the r.f. power increases. Moreover, the cathodic branch of the polarization curves is markedly suppressed as the substrate electrodes are covered with films, indicating inhibition of the oxygen reduction reaction, due to the efficient barrier to molecular oxygen diffusion.

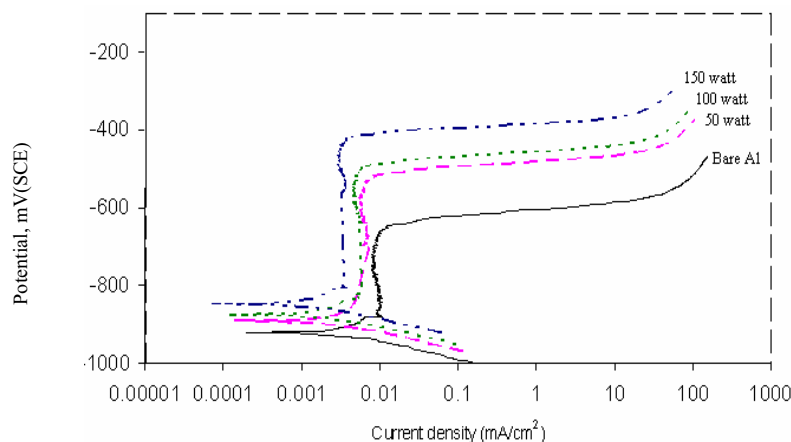


Figure 3: Polarization curves of bare aluminum electrode, and those covered with HMDSO films deposited at various r.f. powers.

This barrier is imposed by the densely packed and tightly interconnected HMDSO films. Simultaneously, the anodic process is also inhibited, suggesting a suppression of the diffusion of metal ion species from the substrate surface as well as the electrolyte active species (Cl^-) to the metal surface. Table (3) presents corrosion potential (E_{corr}),

corrosion current density (i_{corr}) and protective efficiency (P_i) of aluminum alloy both bare and covered with HMDSO films at different r.f. powers obtained from the potentiodynamic curves of Figure (3). The protective efficiency (P_i) of the film was determined from the polarization curves by the Equation [6]:

$$P_i = 100 \times (1 - (i_{\text{corr}} / i_{\text{corr}}^{\circ}))$$

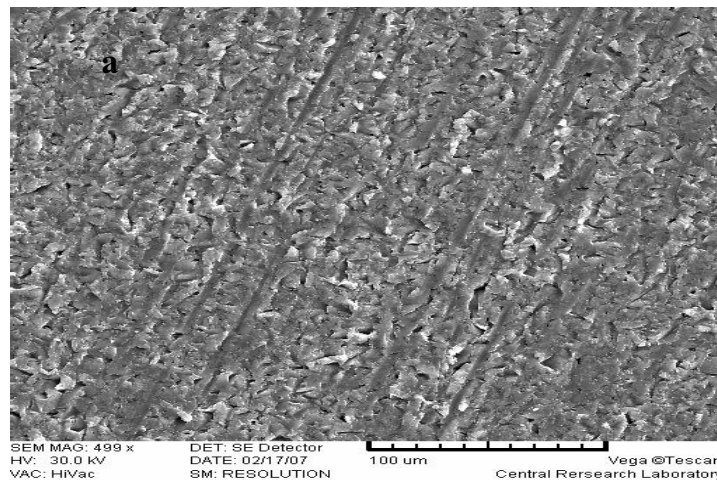
where i_{corr} and i_{corr}° indicate the corrosion current densities with the presence and absence of the film, respectively. As shown in Table (3), the protective abilities of films increased with increasing r.f. powers. The highest protective efficiency was 50 % at 150 Watt r.f. power.

Table 3: corrosion properties of aluminum alloy covered with HMDSO films obtained from potentiodynamic curve

State of electrode	E_{corr} (mV)	i_{corr} (mA/cm ²)	P_i %
Bare Al	- 921.6	0.0012	--
+ coat at 50 watt r.f.	- 897.5	0.0009	25.0
+ coat at 100 watt r.f.	- 866.8	0.0008	33.3
+ coat at 150 watt r.f.	- 830.9	0.0006	50.0

SURFACE MORPHOLOGY

Figures (4a - 4c) show the SEM images of polymer like thin film deposited from HMDSO on Al substrate at different r.f. powers. The images indicate that the surface roughness decrease with increasing r.f. power.



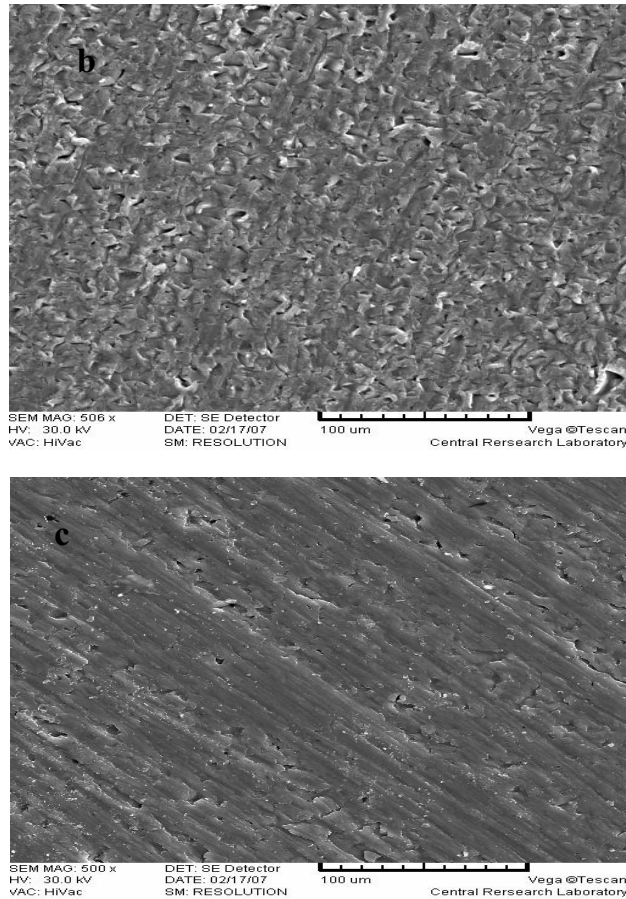


Figure 4: SEM images of polymer like thin film deposited from HMDSO at r.f. power (a) 50 watt, (b) 100 watt and (c) 150 watt.

CONCLUSIONS

Organic polymer thin films were deposited on glass, and aluminum alloy type 6061 substrates at room temperature by plasma enhanced chemical vapor deposition (PECVD) method, using HMDSO as organic precursor. Study of the chemical structure, contact angle, and corrosion protective efficiency of plasma polymerized organic thin films grown at various r.f. powers revealed that with increasing the r.f. power.

- Absorption of hydrogen in the film increases, while that of oxygen decreases,
- The contact angle of the film with the substrate increases,
- The surface roughness decreases,
- The corrosion protective ability of the deposited films against chloride ions in 3.5 wt% NaCl environment increases.

ACKNOWLEDGMENT

This work is financially supported by the National Bureau for research and development and the plasma research laboratory.

REFERENCES

- [1] V. Cech, P. Horvath, J. Jancar, F. Schauer, and S. Necpurek, "Plasma Polymerized DCMPS as Adhesive Film Characterization and Properties", *Chem.* 53 (3), 1999, 165-173.
- [2] S. Gaur, G. Vergason, and Van Etten, "Plasma Polymerization: Theory and Practice", 43rd Annual Technical Conference Proceedings - Denver, April 15-20, 2000.
- [3] D. Shi, P. He, J. Lian, L. Wang, and W. J. van Ooij, "Plasma deposition and characterization of acrylic acid thin film on ZnO nano particles", *J. Mater. Res.*, Vol. 17, No. 10, Materials Research Society, Oct 2002.
- [4] Y. J. Yu, J. G. Kim, and J. H. Boo, "Plasma-polymerized thiophene films for corrosion protection in microelectronic devices", *Journal of Material Science Letters* 21, Kluwer Academic Publishers, 2002, 951– 953.
- [5] S. H. Cho, Z. T. Park, J. G. Kim, and J. H. Boo, "Physical and optical properties of plasma polymerized thin films deposited by PECVD method", *Surface and Coatings Technology* 174 –175, Elsevier Science B. V., 2003, 1111-1115.
- [6] Y.J. Yu, J.G. Kim, S. H. Cho, and J.H. Boo, "Plasma-polymerized toluene films for corrosion inhibition in microelectronic devices", *Surface and Coatings Technology* 162, Elsevier Science B. V., 2003, 161-166.
- [7] J.C.S Fernandes, M.G.S. Ferreira, D.B. Haddow, A. Goruppa, R. Short, and D.G. Dixon, "Plasma-polymerized coatings used as pre-treatment for aluminium alloys", *Surface and Coatings Technology* 154, Elsevier Science B. V., 2002, 8-13.
- [8] A. R. Denes, M. A. Tshabalala, R. Rowell, F. Denes, and R. A. Young, "Hexamethyldisiloxane-Plasma Coating of Wood Surfaces for Creating Water Repellent Characteristics" *Walter de Gruyter, Holzforschung*, 53, 1999, 318-326.
- [9] A. Cremona, L. Laguardia, E. Vassallo, G. Ambrosone, U. Coscia, F. Orsini, and G. Poletti, "Optical and structural properties of siliconlike films prepared by plasma-enhanced chemical-vapor deposition", *Journal of Applied Physics*, 97, 023533, 2005.
- [10] M. L. P. da Silva, I. H. Tan, A. P. Nascimento Filho, E. Galeazzo, and D. P. Jesus, "Use of plasma polymerized highly hydrophobic hexamethyldissilazane (HMDS) films for sensor development", *Sensors and Actuators B* 91, 2003, 362-369.

