

# INFRARED AND X-RAY PHOTOELECTRON SPECTROSCOPY IN SURFACE CHARACTERIZATION OF POLYDIMETHYLSILOXANE THIN FILMS GENERATED ON METALLIC SUBSTRATES IN MULTIPPOINTS TO PLANE CORONA DISCHARGES

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By coupling two spectral techniques, namely, X-ray photoelectron and specular reflection infrared spectroscopy at high reflection angles, we identified, in this paper, the formation of SiO<sub>2</sub> respectively SiO<sub>x</sub> ( $1 < x < 2$ ) structures on the surface of polydimethylsiloxane thin films. These layers have been obtained as a result of placing a thin liquid film precursor on a germanium substrate under corona charge injection in multipoints to plane electrodes configuration in air at atmospheric pressure for 2 hours.

*Key words:* polydimethylsiloxane thin films, corona discharge, specular reflection infrared spectroscopy, XPS spectroscopy.

## 1. INTRODUCTION

Extensively used as protective corrosion media or in medical applications, the polydimethylsiloxanes (PDMS) are characterized by remarkable thermal stability, low surface energy, hydrophobicity, high gas permeability, low permeability to water, and low electrical conductivity, most oxidizing agents not being able to attack their structure due to the strength of the Si–O bonds [1]. Their biologically inertness, elasticity, transparency and compatibility with human tissue recommend them as substrates or matrix materials for medical applications [2, 3].

PDMS layers with surfaces functionalized by different methods like oxygen plasma or ultraviolet-ozone (UV-ozone) treatments became more SiO<sub>2</sub> like surfaces with more –OH groups and are extensively used for cell adhesion or antibacterial activity test experiments [4].

In our previous papers [5, 6], we showed that PDMS layers generated in atmospheric pressure corona discharges in a point to plane electrode configuration starting from different thin films of liquid precursors placed on the plane electrode, are more SiO<sub>2</sub> like surfaces. The Si-OH groups identified in the PDMS layers at its surface [7], bulk [8] and at polymer-substrate interface [7–10] can improve the adherence of the polymer to substrate surface, thus avoiding the polymer delamination due to the formation of interlink bonds of Si-O-Metal type. The contribution of the PDMS layers to the improvement of the adherence and mechanical properties of silver doped hydroxyapatite coatings has been recently proved in [11]. It has also been showed that the silver doped hydroxyapatite/polydimethylsiloxane composite layer could prevent or lag the fungal biofilm development [12], being of a great interest in the biomedical field.

In the present work, by specular reflection infrared and X-ray photoelectron spectroscopy we investigated the type of silicon oxides formed at the surface of a PDMS layer generated by placing a thin liquid film precursor on a germanium substrate in a multipoints to plane corona discharge produced in air at atmospheric pressure.

## 2. EXPERIMENTAL CONDITIONS

In [8] we reported the generation of solid polymer layers in corona discharges in a point to plane electrodes configuration starting from PDMS thin liquid film precursors. In such configuration, only a drop of 0.1  $\mu\text{l}$  PDMS liquid precursor stretched on an Al substrate was transformed into a solid polymer layer after 2 hours.

In the present work we overcome this problem by using multipoints (7 tungsten wires) to plane corona discharge electrode configuration for the polymerization of PDMS liquid precursors. Thus, for different volumes of the liquid precursor (0.1–0.7  $\mu\text{l}$ ) solid polymer layers were obtained after 2 hours of running corona discharge.

The new electrode configuration of the corona discharge consists in a central tungsten wire placed at 12 mm perpendicular to the center of the disk electrode (20 mm diameter) and 6 wires placed at 15 mm from the plane electrode and distributed so that they can be regarded as the peaks of two equilateral triangles sharing the same center, namely the 7<sup>th</sup> wire. The electrodes lie under a glass cage and a DC high voltage of 11 kV applied through a 5 M $\Omega$  resistor determines a mean current of 25  $\mu\text{A}$  as well as a Trichel pulsed regime of the negative corona discharge (the time period being of 1.3  $\mu\text{s}$ ).

The pulsed current assures a uniform and periodic charge transport between electrodes. A high DC negative voltage applied to one sharp electrode ionize the surrounding air creating charged particles distributed as clouds drifting along the

electric field lines. The geometric configuration of a point to plane corona discharge and the occurrence of such clouds determine a strongly non-uniform electric field between electrodes that varies with time as successive clouds drift from one electrode to the other [8].

The uniformity of the current density distribution on the plane electrode was experimentally determined for the first time by Warbung in 1899. Sigmond [13] established that the uniformity of the current density distribution on the plane electrode in a Trichel pulsed regime can be obtained on a circular surface with the radius  $r = \sqrt{3} d$ , where  $d$  is the interelectrode gap. In a point to plane corona discharge configuration  $r = 17.2$  mm [8]. Thus, the current density is uniform over a circular surface of maximum 20 mm in diameter on the plane electrode.

In case of the multipoints (7 tungsten wires) to plane corona discharge electrodes configuration we have experimentally investigated the current density distribution on the plane electrode by optical analysis of the influence of active species produced in corona discharge on the substrate. In Fig. 1 can be observed the central zone of the plane electrode deposited with a thin layer of PDMS on a surface of about 1 cm (Fig. 1a) and about 2 cm (Fig. 1b).

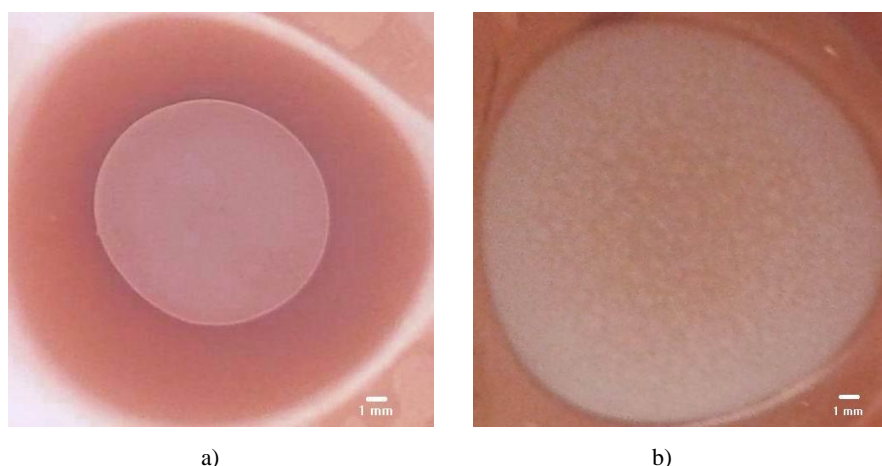


Fig. 1 – PDMS layer deposited in multipoints to plane corona discharge electrode configuration starting from: a) 0.1  $\mu$ l; b) 0.5  $\mu$ l; PDMS liquid precursors.

Surface investigations of PDMS thin films deposited on germanium substrates in a multipoint to plane corona discharge electrodes configuration have been performed by reflection FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS) a high sensitivity technique suited for the composition surface chemical states evaluation.

### 3. FT-IR INVESTIGATIONS

Reflection spectroscopy is a versatile technique for providing spectroscopic information of thin films as there is no necessary sample preparation or their dilution in non absorbing matrices as is the case of transmission spectroscopy [14].

In [7–9], the PDMS layers deposited on metallic mirror like surfaces in point to plane corona discharges were investigated by reflection IR spectroscopy.

The reflection-absorption IR spectra of the PDMS layers deposited on aluminum mirror like surfaces were recorded by the variable angle specular reflectance accessory positioned inside the IR spectrometer by varying the angle of light incidence on the sample within the range of 30° to 60° [8]. Using this technique as the light passes through the surface layer twice, the intensity of the IR bands in the IR spectrum increases. The optical path and the penetration depth of the light into the layer can be modified by varying the angle of light incidence onto the sample.

In [5–10] has been proven that during the polymerization process of a thin film of PDMS liquid precursor placed on the plane electrode in corona discharge, some SiO<sub>2</sub> like structures are generated. The type of SiO<sub>2</sub> structures and their distribution in the polymer layer was determined by different complementary methods to FTIR spectroscopy such as Glow Discharge Optical Emission Spectroscopy (GDOES), Plasma Profiling Time of Flight Mass Spectrometry and Scanning Electron Microscopy. The GDOES depth profiling analysis of PDMS layers [7–9] was in good agreement with the reflection IR spectral studies performed for an angle of incidence of the light on the sample of 30°, revealing not only the absorption IR bands specific to PDMS but also indicating some associated processes, respectively the chemical bonds formed at polymer-substrate interface. Hence, the analysis of the IR spectra recorded for reflection angles ranging between 30–60° and the GDOES depth profile curves of Si, O, C, H elements indicate that the density of the silicon oxides structures formed in the PDMS layer increases toward the polymer surface [7, 8].

This paper presents the results obtained by specular reflection measurements using a SP100 IR Perkin Elmer spectrometer equipped with a variable angle specular reflectance accessory and a SPECTRUM acquisition software. The angle of incidence of light on the sample was 80°. As known, for higher incidence angles ranging from 60°–85°, the contribution of the reflected light on the upper surface of a thin film to the IR spectrum is better evidenced [15]. The recorded IR reflection spectrum was converted into an absorption one using the Kramers-Kronig transformation of the SPECTRUM software.

Figure 2 presents the IR absorption spectrum of a PDMS layer recorded at an incidence angle of light on the sample of 80°. The absorption bands observed at ~ 1120, 830, and 490 cm<sup>-1</sup> are attributed to asymmetric stretching, symmetric stretching respectively bending vibration of Si–O–Si bond of SiO<sub>4</sub> tetrahedral units

[16, 17]. The IR band from  $1050\text{ cm}^{-1}$  was assigned to Si-O bond vibrations inside of some approximately  $\text{SiO}_{1.5}$  structures [18]. Some other bands like Si-OH ( $980\text{ cm}^{-1}$ ) vibrations or Si-O-Si ( $540\text{ cm}^{-1}$ ) stretching vibrations inside the silica network can also be observed [19].

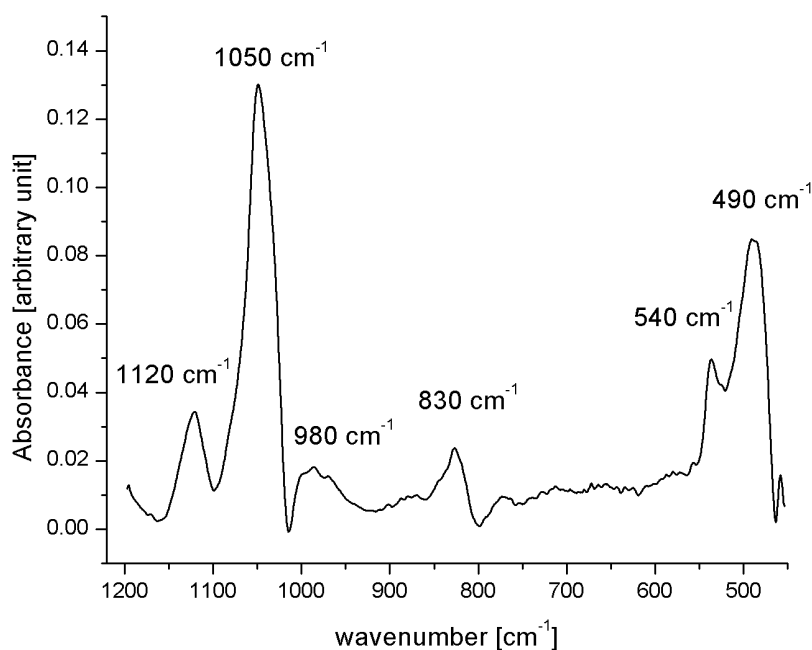


Fig. 2 – FTIR spectrum of the PDMS layer obtained for an angle of the incidence light on the sample of  $80^\circ$ .

#### 4. XPS INVESTIGATIONS

As already known, in XPS technique the photoelectrons emitted from the topmost surface (typically 1–10 nm) of a material bombarded with X-rays, yield specific binding energies of the chemical elements. Thus, small changes in the chemical bonding environments result in small shifts in the photoelectron energy, thus allowing chemical information to be obtained. For example, from the binding energies, the oxidation state, the nearest neighbor atoms and the type of bonding may be evaluated.

The present study is focused on the Si 2p and O 1s XPS spectra of the PDMS layers out of which we can extract information on their chemical bonding and composition.

The XPS measurements were performed with a SPECS installation using a monochromatic X ray source with Al anode ( $E_{K\alpha} = 1486.61$  eV). The pressure value within the vacuum analysis chamber was  $p \sim 3 \times 10^{-9}$  torr. The XPS recorded spectrum for Si 2p and O 1s spectral lines, involved a pass energy of 20 eV and an energy window  $w = 20$  eV with 400 recording channels, each channel being characterized by a 0.05 eV width. The extended spectrum was recorded with pass energy of 50 eV for a 0.5 eV channel width. The measured binding energy (EB) scale was referenced to a C 1s at the EB value of 284.8 eV [18]. The accuracy for BE's assignments is  $\pm 0.2$  eV. The XPS spectra were processed using Spectral Data Processor v. 2.3 (SDP) software.

Figures 3 and 4 present the wide scan energy spectrum of the PDMS layer respectively the high resolution XPS spectra of the Si 2p and O 1s lines.

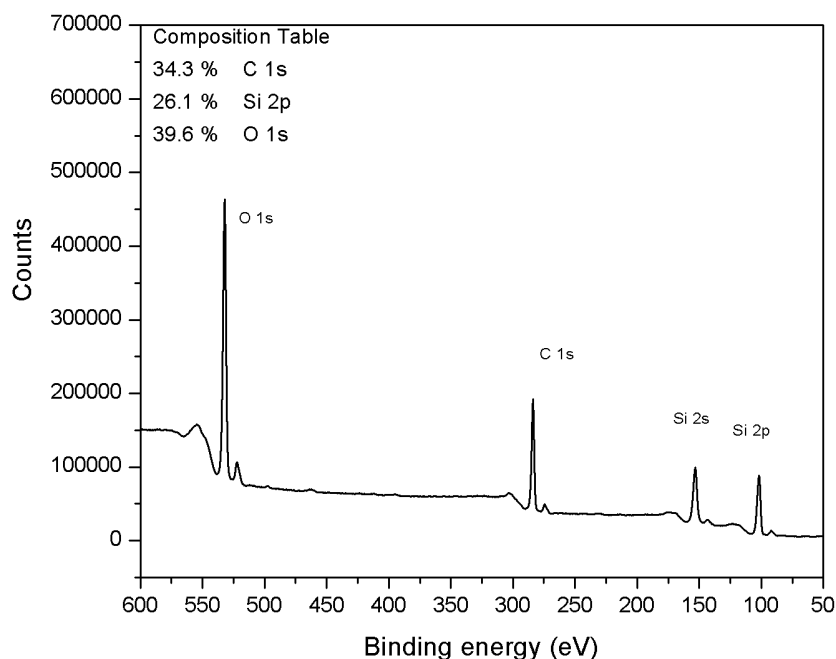
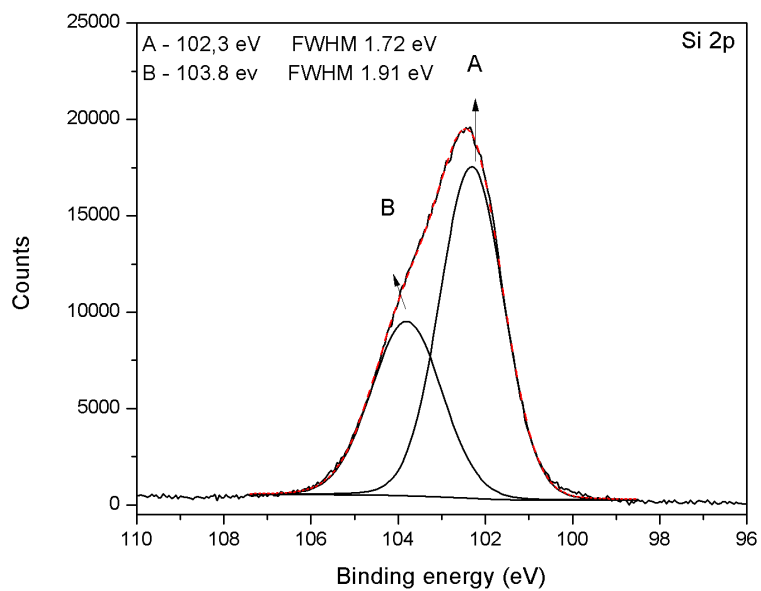
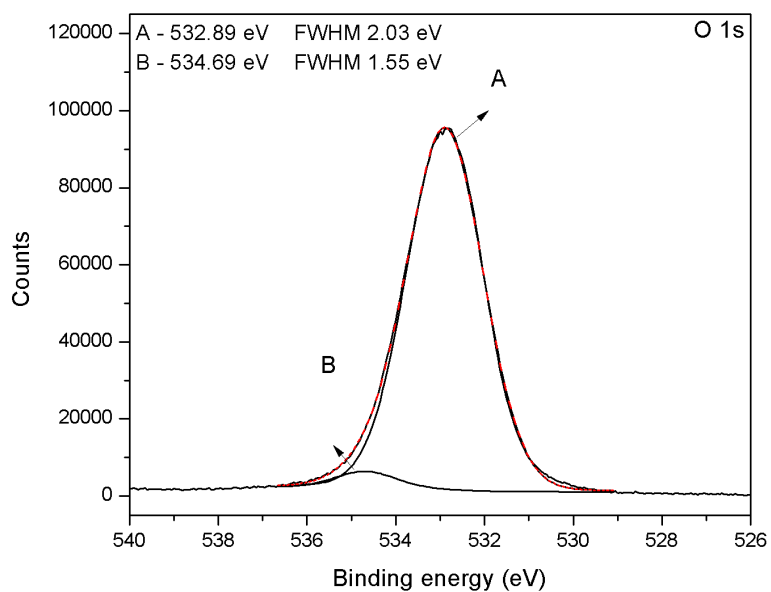


Fig. 3 – XPS wide scan energy spectrum of the PDMS layer.

The peak fitting analysis of the Si 2p XPS peak was performed with Spectral Data Processor software using the Voigt functions (with a 90/10 Gaussian/Lorentzian ratio) and Shirley background subtraction method. The sensitivity factors provided by the spectrometer manufacturer have been used for quantitative analyses.



a)



b)

Fig. 4 – High resolution XPS spectra for (a) Si 2p, (b) O 1s. The experimental curve is plotted in black and the theoretical fitted curve is in red dot line.

The 102.3 eV and 103.8 eV Si 2p deconvoluted XPS peaks are specific to SiO<sub>2</sub>-like compounds binding energies, indicating a SiO<sub>1.19</sub> respectively a SiO<sub>2</sub> compound formation [20]. The peak A represents 63.1 % and the peak B 36.9 % from experimental curve. The two Si 2p peaks observed in Figure 4 presents a FWHM of 1.72 eV (102.3 eV) respectively 1.91 eV (103.81 eV).

The O 1s peak identified at 532.89 eV reveals the silicon dioxide formation while the 534.87 eV deconvoluted band indicates the presence of Si-OH groups on the PDMS layer surface. Although H<sub>2</sub>O is easily adsorbed on the surface of the inorganic polymer samples, physically adsorbed H<sub>2</sub>O molecules are easily desorbed under ultrahigh vacuum conditions characteristic to a XPS system. Therefore, hydroxyl presence on the surface of the sample can be attributed to the silanol groups from the polymer layer [21].

## 5. CONCLUSIONS

Due to the increase of the surface charge density on the substrate achieved in the electrode configuration of multipoints to plane (substrate) corona discharge produced in air at atmospheric pressure, polymerization of different volumes of thin film liquid precursors occurs.

The FTIR and XPS spectral methods used for the characterization of the PDMS films deposited on the germanium substrates indicate beside SiO<sub>2</sub>, some specific silicon oxide structure of SiO<sub>x</sub> (1 < x < 2) type. The similarity of results obtained by these two methods revealed that specular reflection FTIR spectroscopy at higher angles of incidence (80°) could be a reliable method for the identification of the chemical bonds present on a PDMS layer surface, giving data in agreement with those provided by the XPS spectroscopy.

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