Research Article

Characterization of the Oxides Present in a Polydimethylsiloxane Layer Obtained by Polymerisation of Its Liquid Precursor in Corona Discharge

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By combining the reflection-absorption infrared spectral studies with the peak fitting analysis we determined the type of the silicon oxides present in polydimethylsiloxane layers obtained on germanium and aluminium substrates in corona discharges. We have also evidenced that the dependence of silicon oxides density on the corona discharge current intensity is related to the existence of a concurrent anodizing process occurring at the polymer/Al substrate interface. The morphology of the Al substrate surface investigated by scanning electron microscopy proved that the anodizing process occurs.

1. Introduction

Polydimethylsiloxanes (PDMS) are widely used as protective corrosion media or in medical applications. The strength of the Si–O bonds gives them a remarkable thermal stability, most oxidizing agents not being able to attack their structure. They are elastic, transparent, and compatible with human tissue and are biologically inert [1].

The PDMS layers are known for their hydrophobic character, although for biomedical applications regarding cell adhesion [2] or antibacterial activity [3] it is important that PDMS layers have a hydrophilic character. By oxygen plasma, water vapor plasma, or ultraviolet-ozone (UV-ozone) treatments their surfaces can be functionalized [4] becoming more SiO_2 like surfaces with more –OH groups [2–5]. Recently [6], it was shown that SiO_2 layers, which have an excellent compatibility with the living tissues, can be used as interlayers for improving the delamination of hydroxyapatite (HAP) [7] coatings.

In our previous papers we presented a method of generation of PDMS layers on different substrates in corona discharges starting from different liquid precursors [8–10]. In [11] we showed by Fourier transformer infrared spectroscopy, glow discharge optical emission spectroscopy, and scanning electron microscopy that function of the liquid precursor end group and substrate material, in the polymer bulk, mainly on the polymer surface, on some SiO_2 like structures can be generated.

In the present work, by peak fitting analysis of the reflection-absorption infrared (IR) spectra of the PDMS layers we have investigated the type of silicon oxides formed in the polymeric layer function of corona discharge current intensity and substrate material. Also, by scanning electron microscopy (SEM) we have analyzed the morphology of the substrate surface after the complete removal of the polymer layer.

We showed that the reflection-absorption IR spectral analysis could be used for the investigation of thin films deposited on different substrates, highlighting the processes occurring at thin film/substrate interface. The understanding of these interfacial processes can be useful in the studies of the different mechanical properties of thin polymeric layers, like adherence. For example, the interlinked bonds performed by the Si–OH groups can improve the adherence of thin layers to substrate surfaces avoiding the polymer delamination.

2. Materials and Methods

In this paper, using a SP100 IR Perkin Elmer spectrometer (with a resolution of $4\,cm^{-1}$) and a SPECTRUM acquisition software version 6.4.1, we investigated by reflection-absorption and transmission IR spectroscopy the PDMS layers deposed in corona discharges on germanium and aluminium mirror like surfaces.

The PDMS layers have been obtained in negative corona discharges in a point (cathode) to plane (anode) electrode configuration (10 mm interelectrodic gap) in air at atmospheric pressure for different values of current intensity (10 μA and 40 μA), starting from liquid precursors of hydroxyl terminated polydimethylsiloxane. These experimental conditions are proper for operating of the negative corona discharge in a Trichel pulse regime known for its uniformity of the current density distribution on the anode surface. Also, in this regime, the pulsating nature of the current assures uniform and periodically charged species (O_2^-, O_3^-, O_4^-, CO_2^-, and CO_3^-) transport between electrodes [11].

The procedure of PDMS thin film generation was as follows: a drop of hydroxyl terminated PDMS lying on the plane electrode is uniformly stretched in a liquid film under the injection of the negative ions produced in corona discharge. The electrohydrodynamic instabilities induced in the liquid film determine the formation of some stationary convective structures of Bernard cell type [8]. Consequently, after 2 hours of corona charge injection on the free surface of the liquid film, a solid PDMS layer, in our case with an average thickness of few hundred of nanometers [11], is generated.

It is well known that specular techniques provide reflectance measurement for reflective materials and reflection-absorption measurement for thin films deposited on reflective surfaces. In reflection-absorption measurements, a part of the radiation is reflected on the upper interface and contributes towards the spectrum via specular reflection. Another part of the radiation penetrates the surface film and is reflected by the reflective surface and, thus, the light passes through the surface layer twice, leading to an increase in intensity of the reflectance spectrum as compared to the normal transmission. The path length of the light through the sample depends on the angle of incidence [12].

In order to get information about the molecules bonds arrangement in the polymer layer and as close as possible to its surface, we recorded the reflection-absorption IR spectra of the PDMS layers deposited on germanium and aluminum mirror like surfaces using a variable angle specular reflectance accessory positioned inside the IR spectrometer. This accessory allows the variation of the angle of incidence of the light on the sample. The path length of the light and consequently the penetration depth of the light into the layer can be changed by varying the angle of incidence light on the sample. The reflection-absorption measurements were performed by varying the angle of reflection in the range of 30˚–60˚ [13].

The acquired reflection-absorption and transmission IR spectra were transformed into absorption spectra according to the formulas $A = \log(1/R)$ and $A = \log(1/T)$, respectively, using the SPECTRUM software.

In order to better reveal the structure of the obtained absorption spectra of the PDMS layers we proceed with the peak fitting analysis performed using the MagicPlotPro software specialized for these kinds of investigations in accordance with the National Institute of Standard and Technology (NIST) [22]. The procedure consists in a baseline correction of experimental IR spectrum followed by the calculation of the second order derivative for peak wavenumbers identification.

For each identified peak we used a Lorentz type profile curve as fitted curve. In the peak fitting analysis process, a sum of all the Lorentz fitted curves is generated by multiple iteration of the nonlinear least squares data fitting algorithm of the software. If the sum of all the fitted curves is set correctly the algorithm gives a valid and convergent solution. The theoretical curve, obtained as a result of peak fitting analysis versus experimental IR curve, will be presented and analysed in our further discussions.

3. Results and Discussions

Our previous papers have shown that, during the polymerization process of hydroxyl terminated polydimethylsiloxane liquid precursors in corona discharges, some SiO_2 like structures are generated. The morphology of these layers deposited on different substrates and their elemental depth profiles [11] showed that the SiO_2 structures are formed in the polymer bulk, mainly on the polymer surface.

In this work, the silicon oxides type in the polymeric layer was revealed by the peak fitting analysis of their reflection-absorption IR spectra. Also, the influence of the anodization process of the substrate on the IR reflection-absorption spectra of the PDMS layers will be analyzed.

3.1. FT-IR Analysis of Polymers Generated on Germanium Substrates. The IR spectra of the PDMS layer generated on a Ge substrate in corona discharge for an intensity of the current of 10 μA are presented in Figure 1. Although there are some differences, both reflection-absorption, Figure 1(a), and transmission, Figure 1(b), spectra indicate the same IR bands specific to PDMS layers: 860 and 792 cm^{-1} peaks attributed to Si–CH_3 rocking and Si–C stretching vibrations; 1400 and 1254 cm^{-1} peaks assigned to symmetrical and asymmetrical deformation of CH_3 bonds in Si–CH_3 groups; 1080 and 1015 cm^{-1} peaks belonging to Si–O–Si stretching vibrations [15].

Knowing germanium as a transparent material to the IR light, we record the transmission IR spectrum of the PDMS layer as a marker for a proper identification of the absorption bands from 870, 570, and 750 cm^{-1} belonging to Ge–O–Ge and Ge–OH vibrational groups [10, 20]. The decrease of the intensity of these absorption bands in the reflection-absorption IR spectrum, Figure 1(a), is accompanied by the increases of the Si–O–Ge IR band from 660 cm^{-1} [10] and the evidence of the Si–OH IR band from ~960 cm^{-1} [18]. As the elemental depth profile of a PDMS layers deposited on a Ge substrate previously showed the presence of a germanium oxide at the polymer/substrate interface [10], we suppose
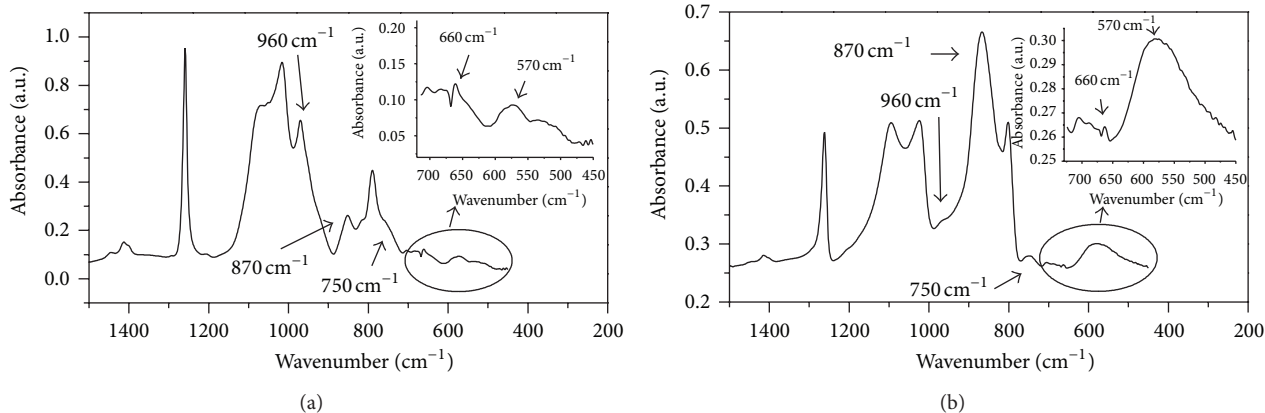
FIGURE 1: IR spectrum of the PDMS layer obtained by (a) reflection-absorption spectroscopy for a reflection angle of 30° and (b) transmission spectroscopy.
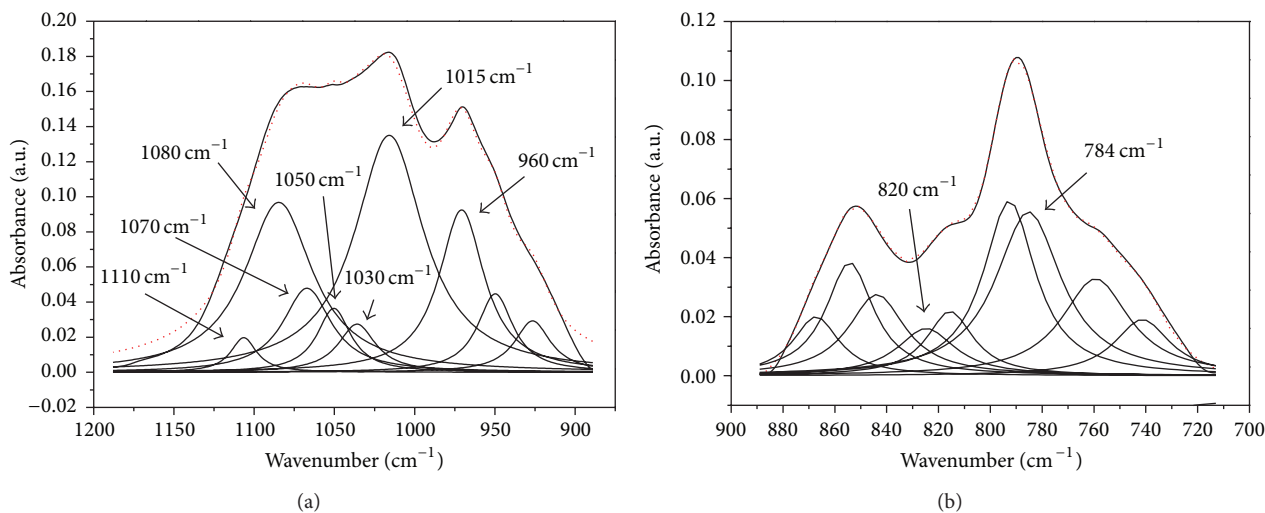

FIGURE 2: Deconvoluted reflection-absorption IR spectra (30° reflection angle) of PDMS layers deposited on Ge substrate in the spectral regions: (a) 1200–900 cm^{-1} and (b) 900–700 cm^{-1}. The experimental curve is plotted in black and the theoretical fitted curve is in red dotted line.

that the IR spectrum obtained for 30° reflection angle can give information about the processes that take place at polymer/substrate interface.

Besides the evidence of the Si–O–Ge interlinked bonds between the polymer layer and the germanium substrate, the strong absorption band of the Si–OH groups present in the reflection-absorption IR spectrum, Figure 1(a), indicates the possibility of the development of some additional processes in the polymer layer, other than the polymerization one.

Therefore, we performed a peak fitting analysis for certain spectral regions of the reflection-absorption IR spectrum from Figure 1(a). This analysis reveals the formation of a SiO$_2$ network with some specific SiO$_{0.5}$, SiO$_{1.5}$, and SiO$_4$ structures in the polymer layer, as is shown in Figure 2 and Table 1.

3.2. FT-IR Analysis of Polymers Generated on Aluminum Substrates.
The PDMS layers deposited on Al substrates in negative corona discharges for 10 μA and 40 μA values of

the discharge current are investigated by reflection-absorption spectroscopy. The peak fitting analysis of the IR spectra obtained for different reflection angles of the light from the sample allowed us to evidence the silicon oxides type: at polymer/Al substrate interface, into the polymer bulk, and as close as possible to its surface, as function of corona discharge current intensity.

In Figure 3 and Table 1 the results of the peak fitting analysis of the IR spectra of the PDMS layer deposited on Al substrate for a value of the corona discharge current of 10 μA are presented. It can be seen that in the spectra of PDMS layers deposited on Al and Ge substrates are identified as the same types of silicon oxides.

Looking carefully at the evolution of the IR bands specific to silicon oxides developed in the PDMS layer function of the reflection angle, Table 1, we can find out the distribution of these structures in the PDMS layer. There are no major increases in the intensities of the IR bands characteristic to

TABLE 1: Identification and characterization of IR bands evidenced in the IR reflection-absorption spectra of the PDMS layers generated on Ge, respectively, Al substrate.

| Wavenumber cm⁻¹	IR bands	Oxide type	Absorbance [a.u'] Ge r = 30°	Al r = 30°	Al r = 40°	Al r = 50°	Al r = 60°
1110	Si–O asymmetrical stretching vibration [14]	SiO$_4$ tetrahedra structures [14]	0.019	0.14	0.55	0.65	0.69
1080	Si–O–Si stretching vibration of the siloxane groups [15]		0.096	0.27	0.27	0.37	0.39
1070	Si–O network stretching vibration [16]	SiO$_2$ network	0.048	0.14	0.16	0.17	0.17
1050	Si–O vibrational group [17]	SiO$_{1.5}$ structures [17]	0.038	0.18	0.26	0.30	0.34
1030	Si–O vibrational group [17]	SiO$_{0.5}$ structures [17]	0.023	0.22	0.26	0.28	0,29
1015	Si–O–Si stretching vibrations of the siloxane groups [15]		0.13	0.31	0.37	0.33	0.34
960	Si–OH vibrational group [18]		0.09	—	—	—	—
950	Si–OH vibrational group [18]		0.04	—	—	—	—
920	Si–OH vibrational group [18]		0.027	—	—	—	—
912	Al–OH vibrational group [19]	Al$_2$O$_3$ [17]	—	0.02	0.02	0.026	0.035
900	Al–O vibrational group [19]		—	0.033	0.026	0.06	0.06
875	Si–OH vibrational group [18]		—	0.040	0.054	0.1	0.11
870	Ge–O–Ge vibrational group [10, 20]	GeO$_2$	0.017	—	—	—	—
860	Si–CH$_3$ rocking vibration [14, 16]		0.037	0.067	0.084	0.11	0.11
852	Si–O asymmetric stretching vibration [14]	SiO$_4$ tetrahedra structures [14]	0.026	—	—	—	—
840	Si–O asymmetric stretching vibration [14]	SiO$_4$ tetrahedra structures [14]	0.026	—	—	0.05	0.06
820	Si–O–Si bending vibration [21]	SiO$_2$	0.015	0.15	0.38	0.51	0.52
815	Si–OH vibrational group [18]		0.021	0.13	0.23	0.31	0.33
792	Si–C stretching vibration [15]		0.059	0.40	0.30	0.28	0.28
784	Si–O symmetrical stretching vibration [14]	SiO$_4$ tetrahedra structures [14]	0.055	0.18	0.18	0.19	0.19
750	Ge–OH vibrational group [10, 20]		0.033	—	—	—	—
740	Si–O/Si–CH$_3$ vibrational groups [14, 16]		0.019	—	—	—	—
660	Si–O–Ge vibrational group [10]			—	—	—	—
570	Ge–O–Ge vibrational group [10, 20]	GeO$_2$		—	—	—	—
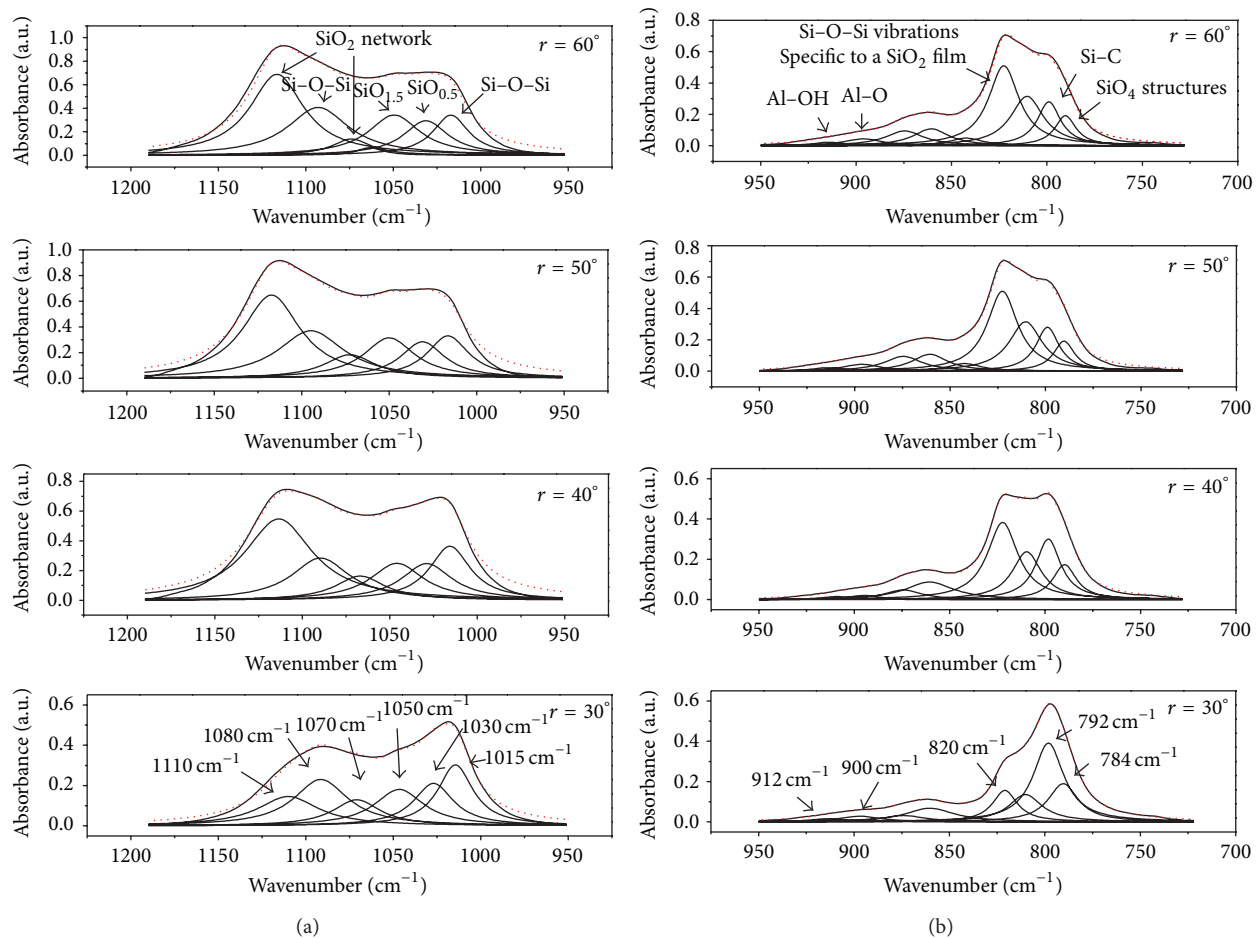
FIGURE 3: The dependence of the deconvoluted IR reflection-absorption spectra of PDMS layers deposited on Al substrate on the reflection angle in (a) 1200–900 cm^{-1} and (b) 900–700 cm^{-1} spectral regions.

siloxane groups (1080 and 1015 cm^{-1}), $SiO_{0.5}$, $SiO_{1.5}$ suboxides (1050 and 1030 cm^{-1}), and SiO_4 (784 cm^{-1}) structures. This fact indicates that the polymerization process of PDMS liquid film and that of the silicon oxides generation in corona discharge are produced homogeneously.
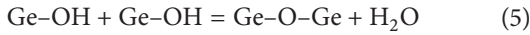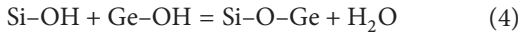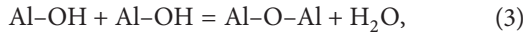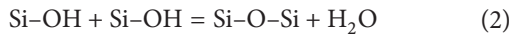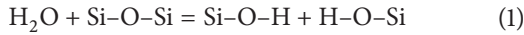
The intensities of the 1110 and 820 cm^{-1} (specific to stoichiometric SiO_2 layers [21]) IR bands increase gradually with the reflection angle mainly due to the higher density of SiO_4 structures formed at polymer surface as the scanning electron microscopy measurements previously showed [11]. In [16], the Si–O vibrations manifested at 1110 cm^{-1} and 1070 cm^{-1} were attributed to a cage like Si–O stretching mode and, respectively, to a Si–O network stretching mode that appears in a SiO_2 network. As the IR bands from 1070 cm^{-1} and 784 cm^{-1} do not present a gradual increase with the reflection angle, it means that at the proximity of the surface a cage like network of SiO_4 structures formation is favored. The results presented in Figure 3(b) and Table 1 also indicate that the intensity of the Si–OH IR band at 875 cm^{-1} increases as we increase incrementally the reflection angle from 30° to 60°. In some previous papers [18] it was shown that the formation of the OH groups on the surface of PDMS layers increases

the bioactivity properties of these materials, making them more proper for biological applications.

The distribution of the Si–O based network in the polymer can be explained if we consider the negatively charged particles deposition at the free surface of the liquid precursor during the polymerization process of the hydroxyl terminated PDMS in corona discharge. The negative ions of oxygen O_2^-, O_3^-, O_4^-, CO_2^-, and CO_3^- and water vapors from the atmosphere [23] are then continuously and uniformly injected into the liquid precursor generating a convective movement of the liquid. In this way, they propagate through the liquid until reaching the substrate. As a result of these processes, the charged particles attack like solvents the chemical structure of the precursor initiating a polymerization process. As the polymerization process advances and the convective movement of the liquid is diminished, the charge particle deposition from the free surface of the material favors the SiO_4 structures formation mainly at the polymer surface [11].

The presence of the polymers deposited on both Ge and Al substrates of the Si–OH, Ge–OH, Al–OH, Si–O–Si, Ge–O–Ge, Al–O–Al, and Si–O–Ge groups in the IR spectra may be considered as a result of the following reactions occurring

in the polymer, respectively [10, 11, 24]:

$$H_2O + Si–O–Si = Si–O–H + H–O–Si \quad (1)$$

$$Si–OH + Si–OH = Si–O–Si + H_2O \quad (2)$$

$$Al–OH + Al–OH = Al–O–Al + H_2O, \quad (3)$$

$$Si–OH + Ge–OH = Si–O–Ge + H_2O \quad (4)$$

$$Ge–OH + Ge–OH = Ge–O–Ge + H_2O \quad (5)$$

Although the PDMS layers are produced in the same experimental conditions on both Ge and Al substrates (10 μA current intensity of the corona discharge), there are no Si–O–Al vibrational bands identified in the IR spectrum from Figure 3.

During the polymerization process of the hydroxyl terminated PDMS liquid precursor in negative corona discharge some water molecules are generated. They can be decomposed under the influence of corona electric fields and associated charge injection, generating OH radicals. Thus, the negative ions of oxygen produced in corona discharge and the OH radicals present in the material bulk can oxidize the substrate surface generating oxides by a process similar to anodization [25]. In a classical electrochemical anodization process, these species are responsible for the oxidation of the material interface and the generation of oxides.

The IR spectra of a PDMS layer deposited on Al substrate in a negative corona discharge for a discharge current of 40 μA are presented in Figure 4. As we increase the reflection angle from 30° to 60° the IR spectra look alike. Although in Figure 4 there are no visible IR bands attributed to Si–O bonds, other than those specific to siloxane groups, the peak fitting analysis allowed the identification of the IR bands characteristic to the SiO$_2$ network. The distribution of these IR bands (for all the reflection angles) is similar to that one presented in Figure 3 in the case of the PDMS layer deconvoluted spectra from 30° reflection angle. This fact could indicate that some concurrent processes that inhibit the major development of the SiO$_2$ network on the polymer layer surface have occurred during the polymerization of the PDMS.

The IR band from 642 cm^{-1}, previously assigned to Si–O–Al bonds formation [11, 26], appears in the spectra in Figure 4, having almost the same intensity for all the reflection angles. This band was not observed in the IR spectrum of the PDMS layer generated on Al substrate for a value of the corona discharge current of 10 μA. It indicates that, at higher values of the corona discharge currents (40 μA), Si–OH bonds are rather involved in the generation of Si–O–Al bonds than in the formation of the silicon oxides.

The dependence of the Si–O–Al IR band intensity on the corona discharge current values observed for a reflection angle of 30° was previously associated with an anodization process of the Al substrate at polymer/substrate interface. The aluminum oxide layer formed at polymer/substrate interface was evidenced by the elemental depth profile of the PDMS layer deposited on an Al substrate for 10 μA corona discharge current intensity [11].
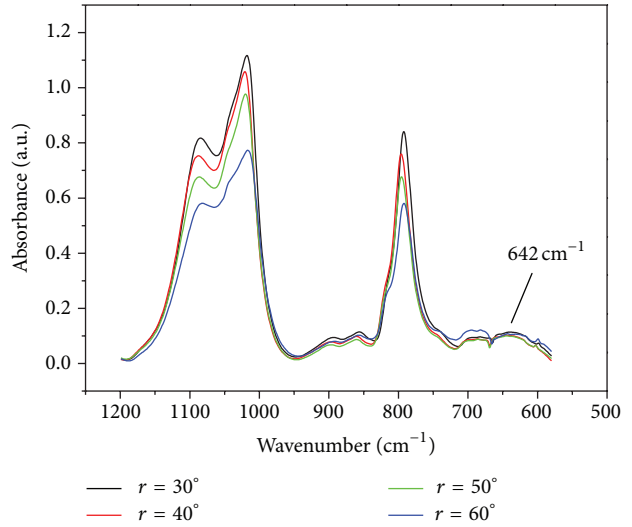

FIGURE 4: IR reflection-absorption spectra of the PDMS layer deposited on Al substrate (at 40 μA discharge current) for different reflection angles.

Therefore, we suppose that the similar values of the Si–O–Al IR band intensities obtained when the reflection angle was gradually increased up to 60° (for 40 μA corona discharge current), Figure 4, could indicate an advanced anodization of the substrate with the formation of some columnar structures [24]. Thus, as the polymer is formed, it follows perfectly the complex surface of the anodized Al interface and the Si–O–Al bonds are uniformly distributed inside the polymer bulk.

The presence of the Si–O–Al bonds in the IR spectrum, Figure 4, indicates that the Si–OH + Al–OH = Si–O–Al + H$_2$O reaction is also possible to occur in the PDMS layer.

3.3. Scanning Electron Microscopy (SEM) Investigation of the Al Substrate Surfaces. The surface morphology of the substrate, after the complete removal of the polymers obtained at two different corona discharge current intensities, was examined using the scanning electron microscopy (SEM). Images were acquired with a FEI Inspect S scanning electron microscope in both high-vacuum and low-vacuum modes.

In Figure 5(a) it can be seen that, for 10 μA intensity of the corona discharge current, the anodized Al surface is rugged with no defined pore structures. On the contrary, when the corona discharge current is increased up to 40 μA, Figure 5(b), the distribution and shape of the pores are changed. Their structure is ordered indicating some columns formation into the material bulk.

These SEM results are in good agreement with the IR spectral analysis shown in Figure 3. In this way, as the polymer is formed it follows the porous surface of the anodized Al substrate, with the Si–O–Al bonds being distributed uniformly into the polymer bulk.

The morphology of the Al surfaces also indicates that the infusion of negative oxygen ions and oxygen based radicals generated in negative corona discharge during the polymerization processes of a PDMS liquid precursor is not limited to
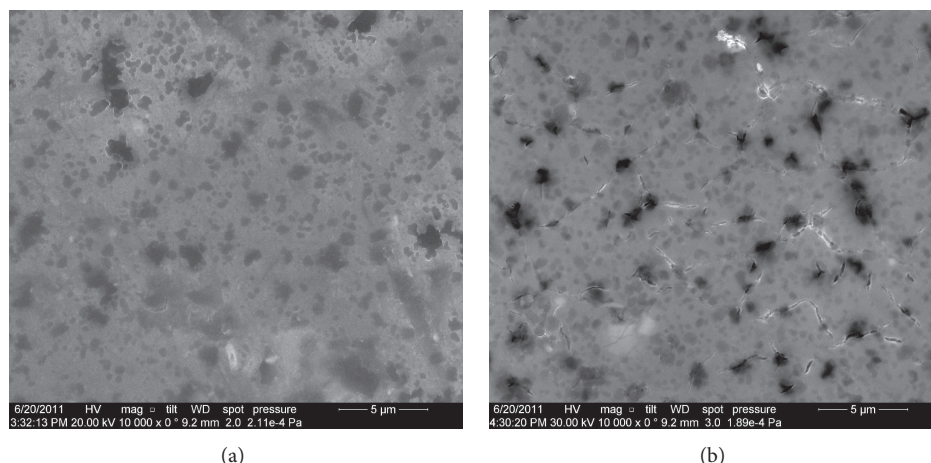
(a)

(b)

Figure 5: SEM images of the anodized Al substrate surface at different corona discharge current intensities: (a) $I = 10\,\mu A$ and (b) $I = 40\,\mu A$.

the polymer surface and polymer bulk, respectively. They can attack directly and indirectly (due to the OH radicals generated into the polymer bulk) the surface of the substrate material by an oxidation process similar to anodization [11, 25].

We did not observe these kinds of structures on the surface of oxidized germanium substrate.

4. Conclusions

The studies performed by reflection-absorption IR spectroscopy coupled with the peak fitting analysis presented in this paper evidenced the type of the silicon oxides structures in the PDMS layer deposed on different supports in corona discharges. At low current intensity of the corona discharge ($10\,\mu A$), the IR spectral analysis of the layers deposed on germanium and aluminium substrates showed that while the $SiO_{0.5}$, $SiO_{1.5}$ suboxides and SiO_4 structures are uniformly distributed in the polymer layer, the cage like network of the SiO_4 structures is more present in the very proximity of the polymer surface. The germanium and aluminium oxides were also evidenced.

As the distribution of silicon oxides structures in the PDMS layer deposed on aluminium substrate is strongly dependent on the corona discharge current intensity, we observed that at high currents ($40\,\mu A$) their distribution is influenced by the anodization of the Al substrate.

The SEM images of the Al substrate surface after the complete removal of the polymers indicate the presence of the porous alumina structures which create the possibility of columns formation into the material bulk. These images evidenced the anodization process of the Al substrate confirming the results obtained by reflection-absorption IR spectral analysis of the PDMS layer.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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