

Article

Depth Profile Analysis of the Modified Layer of Poly(vinyltrimethylsilane) Films Treated by Direct-Current Discharge

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Abstract: Previously, we found that modification of the membrane surface from polyvinyltrimethylsilane (PVTMS) by treatment with low-temperature plasma induced by low pressure DC discharge leads to a significant increase in gas separation characteristics. To understand the mechanism of this phenomenon, in this article XPS combined with precision etching 10 keV beam of Ar₂₅₀₀⁺ clusters was used for depth profiling of PVTMS spin-coated films before and after DC discharge treatment. The etching craters depths were measured by stylus surface profiler. The average etching rate of the untreated PVTMS film by Ar₂₅₀₀⁺ clusters was defined (230 nm/min). It was found that the low temperature plasma treatment of PVTMS leads to a sharp increase in the oxygen concentration on a surface with a simultaneous decrease in the carbon content. The experimental data obtained indicate also that the treatment of PVTMS film by plasma leads not only to a change in the chemical structure of the surface, but also to the formation of a gradient subsurface layer with a thickness of about 50 nm.

Keywords: poly(vinyltrimethylsilane) film; direct current discharge modification; X-ray photoelectron spectroscopy; precision etching; argon gas cluster ion beams (GCIB); depth profile analysis



Citation: Piskarev, M.; Skryleva, E.; Gilman, A.; Senatulin, B.; Zinoviev, A.; Syrtsova, D.; Teplyakov, V.; Kuznetsov, A. Depth Profile Analysis of the Modified Layer of Poly(vinyltrimethylsilane) Films Treated by Direct-Current Discharge. *Coatings* **2021**, *11*, 1317. <https://doi.org/10.3390/coatings11111317>

Academic Editor: Esther Rebollar

Received: 14 October 2021

Accepted: 25 October 2021

Published: 29 October 2021

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1. Introduction

Low-temperature plasma is widely used to modify the surface properties of polymeric materials [1–6]. It is currently believed that the depth of a modified layer of polymers, treated by various kinds of discharges, is in the range from several nanometers to $\leq 1\text{--}2\ \mu\text{m}$. However, we know only a few works devoted to the experimental determination of the depth of the modified layer after plasma treatment of polymers [7–9], although this parameter is very important for understanding the mechanism of plasma action on the surface of polymers.

In 1991, Nakayama et al. [7] reported the determination of the depth of modified layer of a poly(ethylene terephthalate) (PET) 20 μm film after treatment by argon RF-discharge, using XPS in combination with secondary ion mass spectrometry and transmission electron microscopy. The depth of the modified layer was in the range of 3–8 nm depending on the Ar pressure (2–26 Pa).

Recently, we determined the depth of the modified layer of polytetrafluoroethylene (PTFE) μm film treated by DC discharge of air at the anode (pressure of 10 Pa; discharge current of 50 mA; processing time of 60 s) [8]. X-ray photoelectron spectroscopy (XPS) and atomic-force microscopy (AFM) was used in the experiment in combination with Ar ion etching. It was found that the depth of the modified layer was 40–50 nm in this case.

The authors compared the experimental and theoretical data on determination of the depth of the modified layer for a polypropylene (PP) film treated by inductively coupled RF argon plasma [9]. Experimental data, obtained using ellipsometry, ion bombardment etching, and exposure to vacuum ultraviolet radiation, were in good agreement with the simulation results. The experimental depth of the modified layer was from 2 to 25 nm depending on variable parameters.

Using XPS, in combination with precision surface etching argon gas cluster ion beams (GCIB), we attempted to determine the depth of the modified layer of a PET film treated by DC discharge [10]. It is known that the use of this new technique is optimal for compositional depth profile investigations in various polymers. It was found that the experimentally determined depth of the modified layer of PET films, treated by DC discharge at the anode, was ≤ 20 nm. However, data on the depth profile analysis of the films modified by plasma are not presented in the literature, even though such data are very important for understanding the mechanism of the modification process.

Treatment with low-temperature plasma and vacuum deposition from plasma (PECVD) are widely used for the modification of polymer pervaporation and gas separation membranes. One of the most promising membrane materials is polyvinyltrimethylsilane (PVTMS) [11–14]. PVTMS is a glassy polymer ($T_g = 155^0$) with a large internal free volume and, as a consequence, high gas permeability. However, its selectivity is not high. The structural formula of PVTMS is shown in Figure 1.

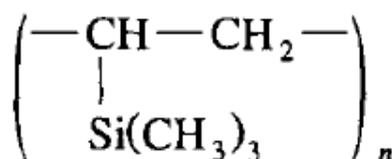


Figure 1. Molecular structure of PVTMS.

In this regard, attempts were made to create an ultra-thin layer of barrier material on the surface of the membranes, which was supposed to increase the selectivity of separation.

Yampolskii Y.P. at all studied the possibility of increasing the gas separation selectivity of PVTMS membrane by forming a thin polymer layer on the surface by plasma-chemical polymerization of $\text{C}_2\text{F}_6 + \text{CH}_4$ mixture using RF-discharge (40.56 MHz) or by fluorination using SF_6 plasma [14]. However, no noticeable effect was obtained.

In [15], it was shown that a modified surface layer, which provides a significant improvement in the pervaporation characteristics of PVTMS membranes, can be formed when the membrane is exposed by glow discharge of industrial frequency (working gas—air).

In our recent work [16], it was found that the effect of a low-temperature DC discharge (working gas—air) on the surface of PVTMS films significantly improves their gas separation properties. After treatment the films at the anode for 30 s, coefficient of selectivity (α_s) of O_2/N_2 gases for PVTMS samples increased from 3.8 to 10.0 without a noticeable decrease in permeability. Considering that, for a large majority of polymers, α_s does not exceed a value of 3–5 [15,17], such approach can be considered as promising one for improvement of gas separation characteristics of PVTMS.

It can be assumed that such a significant change in the diffusion properties is associated with a change in the chemical structure and morphology of the surface layer of PVTMS. The depth of the modified layer depends on the nature of the polymer and the conditions of plasma treatment [7–10]. The experimental values of the depth of the modified layer obtained for several polymers are from 2 to 50 nm.

In connection with the above, it is clear that the layer-by-layer analysis of the chemical composition of PVTMS films, modified by a direct current discharge, is very important for understanding the mechanism of enhancing the selectivity of gas separation.

2. Materials and Methods

The PVTMS films were spin-coated on Si-(C, Ag) substrate using the “Laurell ws 650mz-8npp/ud3” device. The substrate was obtained by vacuum thermal evaporation of Ag nanoparticles and magnetron sputtering of amorphous carbon 25 nm film onto a silicon wafer. A planar structure and a smooth surface containing a chemical element other than the polymer structural elements are the reasons why we chose this substrate. Then, 350 μ L of a 5% PVTMS solution in toluene was applied to the substrate using a syringe. The substrate with the applied solution was spun in three stages: 1—angular frequency $w_1 = 150$ rpm for $t_1 = 1.5$ min; 2— $w_2 = 500$ rpm, $t_2 = 1.5$ min; $w_3 = 1500$ rpm, $t_3 = 30$ s. The resulting coatings were dried in an oven at 80 °C for 15 min.

PVTMS films were treated by DC discharge-induced cold plasma in vacuum using a technique and installation that we described in detail in [18]. Samples were placed at the anode, filtered atmospheric air was used as a working gas, the residual pressure in the system was ~ 20 Pa, the discharge current was 50 mA, and the processing time was 30 s (PVTMS-30A). Only the PVTMS-coated side of the sample was treated by the discharge

A PHI5500 VersaProbeII XPS system (ULVAC-PHI. INC, Kanagawa, Japan) equipped with the Ar_n^+ gas cluster ion beam (GCIB) source was used to record the XPS spectra and perform depth profile analysis. Monochromatic Al $K\alpha$ irradiation with 25 W power and 100 μ m beam diameter was used for photoemission excitation. Atomic concentrations were calculated by the method of relative sensitivity factors. The Si2p and C1s narrow scans were acquired at high resolution (HR) with analyzer pass energy of 11.75 eV and a step size of 0.1 eV. The Binding Energy (BE) scale was calibrated using gold and copper (Au 4f—83.96 eV and Cu 2p₃—932.62 eV). Correction of the BE scale was performed using the Si 2p_{3/2} peak in raw PVTMS sample— 100.5 ± 0.1 eV [19].

The depth profile was analyzed using a 10 keV beam of Ar_{2500}^+ clusters (average cluster size 2500, $E/n = 4$ eV) with a normal angle of incidence. The square raster area was 2 mm²; the current density was 1.3×10^{-6} A/cm². A dual beam flood gun was used for charge compensation.

The GCIB etching rates were evaluated by measuring of the etching craters depths with an Alpha-Step IQ stylus-based surface profiler.

3. Results

3.1. XPS of Initial PVTMS Surface

The atomic fractions, determined on the initial (untreated) PVTMS surface (C—83.0 at. %; Si—15.3 at. %, O—1.7 at. %), approximately correspond to the elemental composition of the PVTMS (C—83.3 at. %, Si—16.7 at. %, excluding hydrogen). Figure 2 shows HR Si 2p and C 1s regions. The main Si 2p doublet 2p_{3/2}—2p_{1/2} (I-I') located at 100.5 eV (BE of Si 2p_{3/2} peak) corresponds to silicon atoms bonded to four carbon atoms in PVTMS, [19]. This component was denoted as Si[4 C]. An additional doublet II-II' of low intensity, located at 101.8 eV, is due to silicon atoms, which have one bond with oxygen; this component was denoted as Si[3C O]. The C 1s region exhibits a single peak located at 284.4 eV, line shape and peak position are consistent with carbon atoms in PVTMS [19].

The experiment on long-term (60 min) irradiation of the polymer surface by 10 keV beam of Ar_{2500}^+ clusters (10 keV Ar_{2500}^+) with current density of 5.8×10^{-6} A/cm² did not reveal any effect on the composition of material.

The binding energies and the shape of Si 2p and C 1s regions did not change, Figure 2, only peak FWHM increased from 0.8 to 1.1 eV for Si 2p I-I' doublet and from 1.0 to 1.3 eV for C 1s. Doublet II-II' Si 2p and oxygen disappeared after the first minute of irradiation.

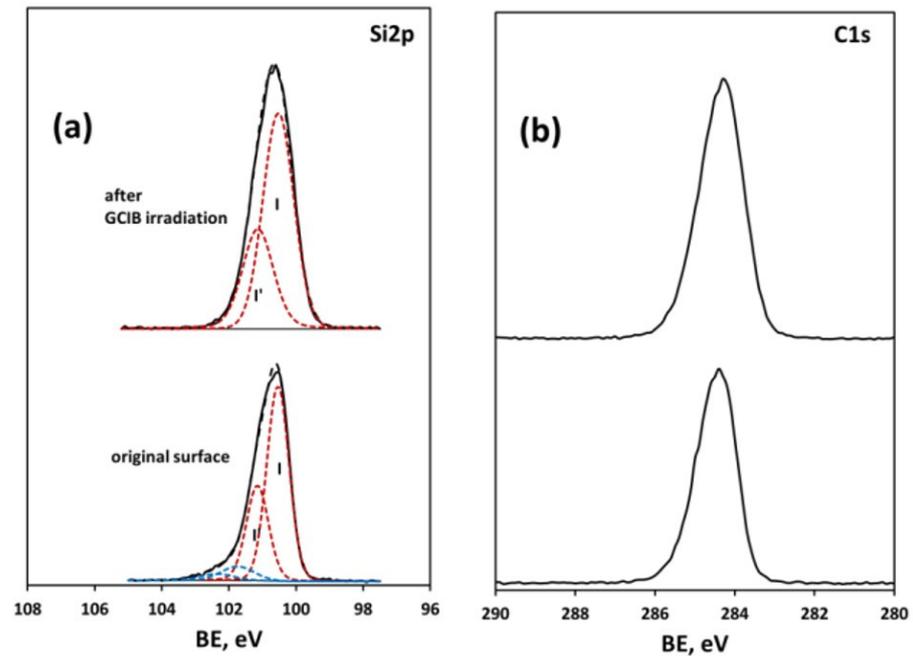


Figure 2. (a) Si 2p and (b) C 1s spectra of the raw PVTMS film for original surface (lower spectra) and after 10 keV Ar_{2500}^+ irradiation for 60 min (upper spectra). Experimental curves—black solid lines; composite curves—black dashed lines; fitted doublet I-I' at 100.4 eV assigned to Si[4C] environment—red dashed lines; fitted doublet II-II' at 101.8 eV assigned to Si[3C O] environment—blue dashed lines.

3.2. The Etching Rate

The etching rate was defined by depth profiling of PVTMS film obtained by spin-coating on silicon substrate with carbon and silver coverage and subsequent crater depth measurement. Figure 3 (left panel) shows the PVTMS—substrate interface at 6–8 min sputter time. Figure 3 (right panel) shows the stylus scan trace of a sputtered crater. The bottom of the crater appears to be too flat, but this flatness is the result of the huge difference between the PVTMS etching rate and the substrate etching rate. Upon reaching the polymer-substrate interface, the etching rate drops sharply, and the peripheral and central parts of the crater are equal in depth. The average value of the crater depth was 1380 nm. Taking into account the etching duration (6 min), the average etching rate of PVTMS was 230 nm/min.

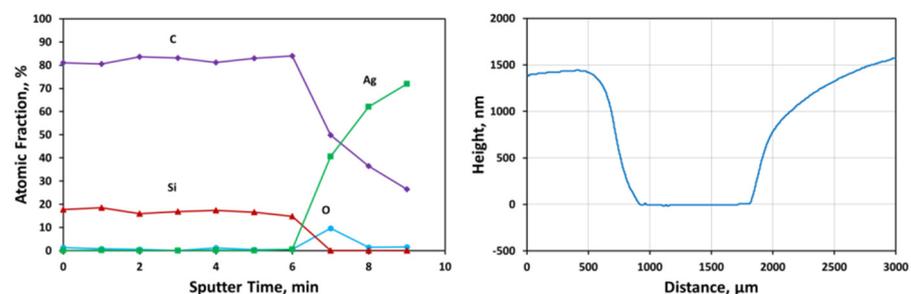


Figure 3. (left panel) Composition of PVTMS film on Si-(C, Ag) substrate as a function of 10 keV Ar_{2500}^+ sputter time and (right panel) crater profile obtained by 10 keV Ar_{2500}^+ sputter for 9 min.

This value of the etching rate is more than 3 orders of magnitude higher than that of inorganic materials under similar etching conditions. For example, the etching rate obtained in the same GCIB mode for LiNbO_3 crystal was 0.094 nm/min [20] and approximately

0.1 nm/min for SiO₂ layer. The obtained experimental data are in good agreement with the results of argon gas cluster sputtering yields calculations in [21]

3.3. XPS of PVTMS Surface Treated by DC Discharge

DC discharge treatment changes the elemental composition of the surface towards a sharp increase in oxygen concentration and a decrease in carbon concentration: O—56.0 at. %; C—24 at. %, Si—20 at. %. Si 2p region exhibits a single doublet located at 103.3 eV, Figure 4a, which indicates silicon atoms bonded to four oxygen atoms. This component was denoted as Si[4O]. BE of the O 1s region is 532.9 eV, which confirms this configuration of chemical bonds as reference BE values of Si 2p and O 1s for SiO₂ are 103.3–103.7 eV and 532.5–533.2 eV correspondingly [22]. The shape of the C 1s line located at 284.9 eV with two additional peaks at 286.7 eV (C-O) and at 289.1 eV (O-C=O) is typical for so called “adventitious carbon”.

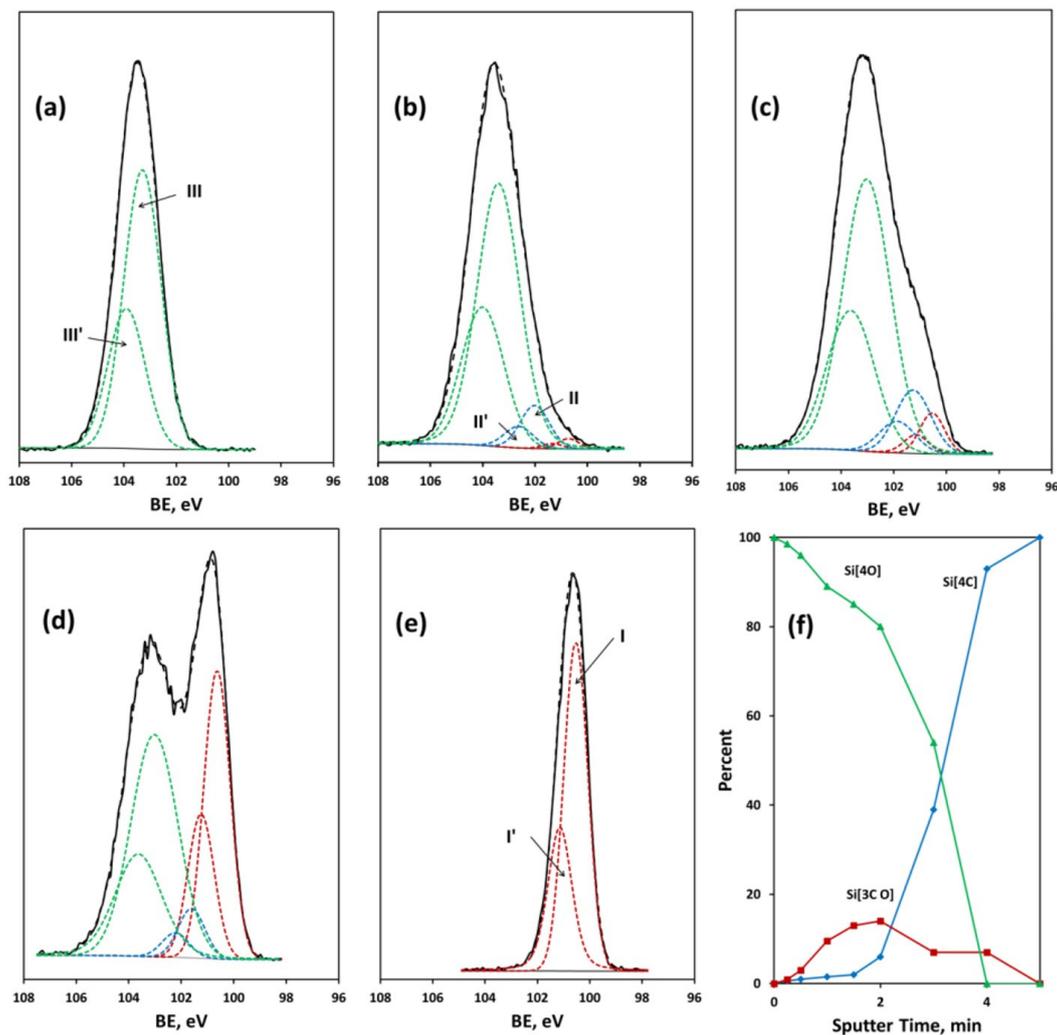


Figure 4. Si 2p region of a 30A sample (a) before sputtering and (b–e) after 1 min, 2 min, 3 min, and 5 min sputtering. Experimental curves—black solid lines; composite curves—black dashed lines; fitted doublet I-I' at 100.4 eV assigned to Si[4C] component—red dashed lines; fitted doublet II-II' at 101.8 eV assigned to Si[3C O] component—blue dashed lines and fitted doublet III-III' at 103.3 eV assigned to Si[4O] component—green dashed lines. (f) Variation in the Si 2p components as a function of 10 keV Ar₂₅₀₀₊ sputter time.

For a more detailed study of the chemical composition of the modified layer, the depth profiling was carried out using 10 keV Ar₂₅₀₀₊ etching. The sample of treated PVTMS (anode 30 s—PVTMS-30A) was analyzed by alternating ion etching and survey and high-

resolution scans at each profile step. Figure 5 (left panel) illustrates compositional depth profile as a function of etching time.

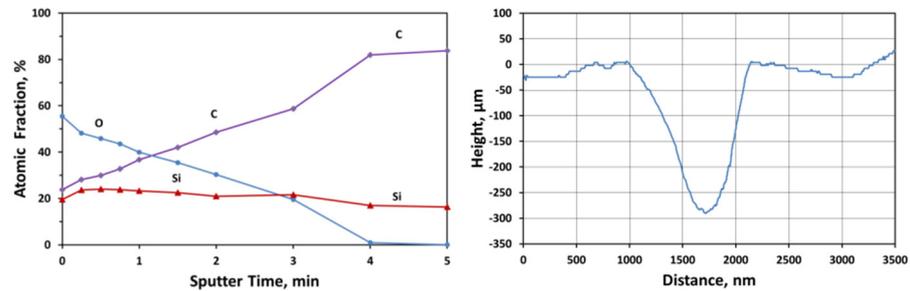


Figure 5. (left panel) Composition of 30 Å sample as a function of 10 keV Ar_{2500}^+ sputter time and (right panel) a profile of the crater obtained by 10 keV Ar_{2500}^+ sputtering for 5 min.

The interval 0–3 min of compositional distribution, with a monotonic decrease in oxygen concentration and an increase in carbon concentration, characterizes a modified layer with variable chemistry. The interval 3–4 min characterizes approaching the treated-untreated layers interphase, and interval 4–5 corresponds to the etching of the virgin polymer. Figure 5 (right panel) shows the corresponding crater profile, obtained after 4 min etching.

Si 2p envelope changed continuously during sputtering. Figure 4a–e demonstrates the evolution of Si 2p region. The region with one component Si[4O] (doublet III-III') was observed only on the surface before etching. The shift of the analysis area into the volume of the modified layer was accompanied by the appearance of the Si[3C O] (doublet II-II') and Si[4C] (doublet I-I') components. The intensities distribution of the Si 2p components over the etching time is shown in Figure 4f.

Figure 6 shows the C 1s region before and after etching. Additional peaks at 286.7 eV and 289.1 eV disappeared after 0.25 min etching, and the main peak shifted to 284.8 eV. This C 1s peak with constant BE and FWHM values up to three minutes of etching is thought to be related to the presence of aliphatic groups in the modified layer. After 2 min of etching, the BE and FWHM of C 1s peak decreases and reaches values of 284.4 eV and 1.3 eV in the 4–5 min section of the compositional profile, corresponding to the zone of untreated PVTMS.

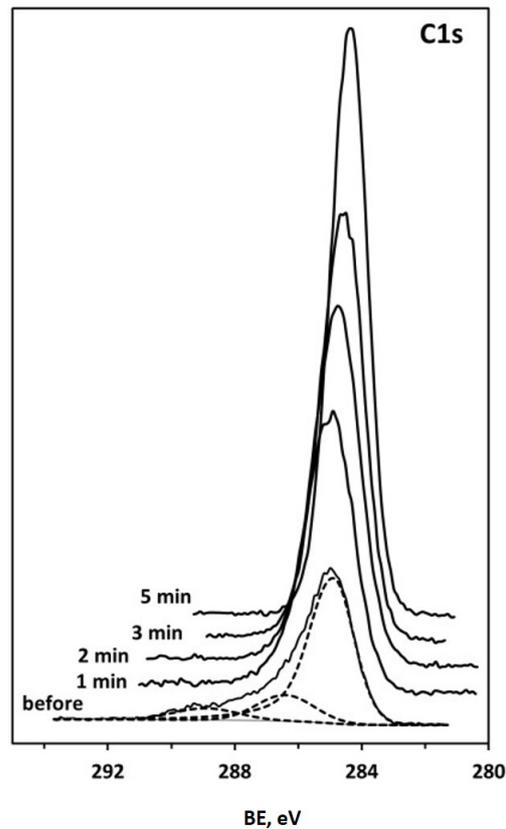


Figure 6. C 1s region of PVTMS-30A sample before and after etching (1 min, 2 min, 3 min, and 5 min).

4. Discussion

As shown in the part 3.3, treatment of the PVTMS film with low-temperature plasma leads to a sharp decrease in the atomic C content on the surface and the appearance of a high atomic O content. The Si content almost does not change, but there is a sharp change in its atomic environment: the uppermost layers of the film show an almost complete transformation of Si–C bonds into Si–O bonds.

To explain these changes, it can be assumed that during plasma-induced chemical reactions, the C atoms of the $\text{Si}(\text{CH}_3)_3$ fragments on the surface pass into the composition of volatile products and are removed from the sample, while Si atoms and C atoms of the main chain also enter into chemical reactions, but they mostly remain in the modified layer. Layer-by-layer analysis of Si2p spectra shows that, with increasing etching depth, the chemical environment of silicon atoms changes. The content of Si atoms in the Si[4O] coordination decreases, and Si atoms appear in the Si[3C O] coordination. These changes are accompanied by a gradual increase in the atomic content of C. The obtained data indicate that the composition of the modified layer continuously changes with depth and gradient. The structure of the modified subsurface layer can be represented as follows (Figure 7).

From Figure 4, on the left, it can be seen that the content of C atoms in the modified subsurface layer increases with increasing etching time. The intensity of the Si[4C] signal also increases (Figure 5f). By the end of the 4-min etching, the spectrum of C1s becomes similar to the spectrum of the untreated polymer. Similarly, the Si[4C] content in the Si2p spectrum does not differ much from the content in pure PVTMS.

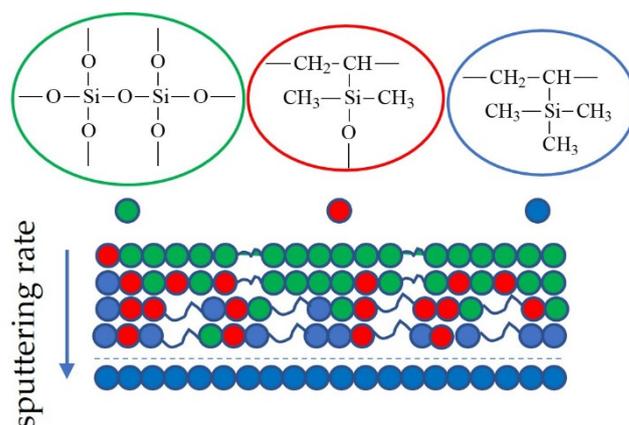


Figure 7. Schematic view of the proposed structure of the modified subsurface layer.

The etching rate seems to be different not only for the modified and unmodified layer but also within the modified layer, depending on the crater lip. Therefore, it is impossible to accurately determine the depth of the modified layer based on the results of the experiment. However, it is possible to make a rough estimate if we accept some assumptions.

The total depth of the crater, formed after 5 min of etching, is 280 nm Figure 4 (right panel). On the other hand, as we can see from Figure 4 (left panel), already after etching for 4 min, the composition of the layer becomes indistinguishable from the composition of the original unmodified PVTMS. Thus, in the interval between the end of the 4th and the end of the 5th minute, pure PVTMS is etched. During this period, the depth of the crater should increase by 230 nm in accordance with the data on the etching rate of the virgin PVTMS (part 3.2). Therefore, by the end of the fourth minute, the depth of the crater must be 50 nm. This value, in our opinion, should be considered the approximate thickness of the modified layer. Although it is impossible to determine the sputtering rate of a layer with a variable composition, it is possible to estimate the average etching rate in this layer from the data obtained. Assuming that the surface of a flat PVTMS sample is covered with a continuous layer with a modified composition, we can estimate the average etching rate in this layer as 12.5 nm/min, which is 20 times less than the rate in PVTMS. Based on the data on the change in the composition of the layers by depth, it can be assumed that the rate should increase with the depth.

The question of the phase morphology of the gradient subsurface layer, and, particularly, the structures of 4-coordinated silicon Si[4O], remains open. Whether they form separate phase particles, or the upper layer of Si[4O] is continuous, whether there is a phase boundary between this layer and the rest is still unknown. The significant increase in the selectivity of gas separation of plasma-modified PVTMS membranes for a nitrogen/oxygen gas pair [16] in our experiments indirectly indicates that the selective subsurface layer, formed during plasma modification, should have a rather continuous structure.

5. Conclusions

Using XPS spectroscopy, the chemical composition of the surface and subsurface layer, formed when exposed to low-temperature plasma generated in a DC discharge on a film of polyvinyltrimethylsilane, was studied. It has been established that such an effect significantly changes the chemical composition of the surface: the atomic carbon content decreases, the oxygen content sharply increases, and the transformation of Si[4C] fragments into Si[4O] occurs. By the method of layer-by-layer etching with argon gas cluster ion beams, with analysis of changes in chemical composition by depth, it was found that the modified subsurface layer has a gradient structure. The depth of the subsurface layer was estimated to be about 50 nm. We believe that formation of the this subsurface gradient layer in PVTMS membranes exposed to DC discharge cold plasma, is a reason for the increasing selectivity of O₂/N₂ gas separation observed by us earlier [16].

Author Contributions: Conceptualization, A.K., A.G., E.S. and V.T.; methodology, E.S., B.S., A.G. and M.P.; software, E.S., B.S., D.S.; validation A.K., A.G., E.S. and V.T.; investigation, M.P.; A.Z., B.S., E.S. and D.S.; resources, E.S., M.P.; A.Z. and B.S.; data curation, E.S., A.G. and V.T.; writing—original draft preparation, A.G., E.S.; writing—review and editing, A.K., A.G., E.S. and V.T.; supervision, A.K., V.T.; project administration, V.T.; funding acquisition, V.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by financial support of the Russian Foundation for Basic Research (Project No. 20-08-00655-a) and by the Ministry of Science and Higher Education of the Russian Federation, topic no. 0086-2019-0007.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: XPS investigations were performed using equipment of the Joint Research Center «Material Science and Metallurgy» NUST MISIS supported by the Ministry of Education and Science of the Russian Federation (project № 075-15-2021-696).

Conflicts of Interest: The authors declare no conflict of interest.

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