

A COMPARATIVE STUDY OF SiO_xC_yH_z THIN FILMS DEPOSITED IN TRIMETHYLSILYL ACETATE/O₂/Ar PLASMAS

Štěpánka KELAROVÁ, Roman PŘIBYL, Vojtěch HOMOLA, Lukáš ZÁBRANSKÝ,
Monika STUPAVSKÁ, Martin ČERMÁK, Vilma BURŠÍKOVÁ

Department of Physical Electronics of Masaryk University, Brno, Czech Republic, EU,
kelarova.s@mail.muni.cz

<https://doi.org/10.37904/nanocon.2019.8643>

Abstract

Plasma-polymerized SiO_xC_yH_z thin films have been playing an important role in many research studies due to their wide range of applications. These materials are perspective for industrial applications as protective coatings of metals or plastic substrates, anti-reflection coatings for solar cells, low-k dielectrics for microelectronics, water-repellent barrier films etc. Materials based on organosilicon precursors prepared by PECVD technique have become interesting for bioapplications in recent years as well due to their ability to optimize protein adsorption and cell attachment. These coatings have a great potential e.g. in BioMEMS microfabrication or treatment of biosensors and surfaces of medical implants.

In the present study, low pressure RF capacitive coupled discharge in mixture of trimethylsilyl acetate (TMSA) monomer with oxygen or argon was used to create hydrophobic SiO_xC_yH_z coatings. This study is focused primarily on research of properties of resulting coatings (chemical composition, mechanical properties, optical properties, surface wettability and surface structure) in dependence on discharge parameters. Properties of created thin films were examined in dependence on the ratio of TMSA monomer and carrier gas flow rates during the deposition process. Influence of used carrier gas (O₂ or Ar) on growth of TMSA-based plasma polymers is discussed in this study as well.

Keywords: Plasma polymers, trimethylsilyl acetate, PECVD, FTIR, microindentation, confocal microscopy, ellipsometry

1. INTRODUCTION

The use of organosilicon-based coatings prepared using plasma techniques in many industrial fields (e.g. protective coatings, anti-reflection coatings, barrier films, superhydrophobic surfaces etc.) [1-5] explains persistent interest in their research and development over the years. Interaction of SiO_xC_yH_z surfaces with biological agents (e.g. as proteins, enzymes, cells) have been intensively examined in recent years in order to apply these materials also in the medical fields [6-8].

Desired properties of organosilicon material are achieved by optimization of deposition process, including the choice of proper precursor, carrier gas (Ar, O₂, N₂ etc.) and other factors of used discharge [1-9]. Hexamethyldisiloxane (HMDSO), trimethylsilane (TMS), tetramethyldisiloxane (TMDSO) and tetraethoxysilane are among the most widely used monomers for preparation of organosilicon materials. The present work is focused on preparation and characterization of plasma polymers based on trimethylsilyl acetate (TMSA) monomer using plasma of RF capacitive coupled discharge. This precursor is, similarly to HMDSO and other commonly used chemicals, suitable for formation of hydrophobic coatings as well as for hydrophilic materials with SiO₂-like structure for industrial applications. Besides Si-CH_x and Si-O bonds occurring in commonly used precursors, structure of TMSA described by linear formula CH₃CO₂Si(CH₃)₃ includes C-C=O group. Possible integration of carbonyl functionalities into resulting coatings during plasma polymerization makes development of TMSA thin films very perspective for medical applications. The aim of the present study is to find relationships between the properties of TMSA-based coatings (chemical composition, mechanical properties,

surface wettability etc.) and the variable discharge parameters. It was proven, that usage of different types of carrier gases leads to the significant differences in structure of organosilicon coatings [1,9]. Therefore, several mixtures of oxygen or argon carrier gases with TMSA monomer were used for preparation of TMSA films. The main focus of the present work was on study of the influence of TMSA precursor amount in gaseous mixture on the properties of resulting coatings as well as on the comparison of the growth of thin films using different carrier gases.

2. EXPERIMENTAL DETAILS

Organosilicon thin films were prepared in RF glow capacitive-coupled discharges at low pressures (~33 Pa) from mixture of TMSA and oxygen or argon in a parallel plate reactor. The bottom electrode served as the silicon substrate holder and it was coupled to RF generator (13.56 MHz) via a blocking capacitor. The supplied power was kept at 50 W for all depositions and flow rates of TMSA and O₂/Ar gas were changed. Changes of the flow rates are represented by the percentage ratio R of TMSA in gaseous mixture given by equation (1), where q_C and q_{TMSA} means the flow rate of carrier gas and flow rate of TMSA in sccm.

$$R = \frac{q_C}{q_C + q_{TMSA}} \quad (1)$$

Properties of the prepared films were studied by several characterization methods. The chemical composition of the resulting coatings was investigated by Fourier transform infrared spectroscopy (FTIR) using spectrometer Bruker Vertex 80v, in range from 370 cm⁻¹ to 7500 cm⁻¹ with 500 scans and resolution of 8 cm⁻¹. Chemical composition of the surface was determined by X-ray photoelectron spectroscopy (XPS). XPS spectra of studied films were measured using Escalab 250Xi device (ThermoFisher Scientific) and Axis Supra spectrometer (Kratos Analytical). Signals of Si 2p, C 1s and O 1s were detected and used for determination of atomic composition of appropriate elements. Si 2p and C 1s peaks were fitted in CasaXPS program to determine concentration of specific bonds. Degree of surface hydrophobicity of each coating was determined by water contact angle measurements using Krüss DSA 30 device. Surface topography was observed by confocal laser microscope LEXT OLS4000.

The thicknesses of thin films and optical constants were determined by non-destructive ellipsometric method. All ellipsometric data were measured by Jobin Yvon UVISEL equipment at angle of incidence equal to 65° in the spectral range from 1 eV to 5.5 eV. Measured data were fitted in the program newAD by using PJDOS dispersion model [10] including anisotropic thin film with wedge-shaped nonuniformity, transition layer and silicon substrate. Mechanical properties were examined using indentation techniques. Measurements of Martens hardness HM , indentation hardness H_{IT} and effective elastic modulus E_{eff} ($E_{eff} = E/(1-\nu^2)$, where E is the Young's modulus and ν is the Poisson's ratio) were realized using Fisherscope H100C microindenter (with maximum load of 1N) and Hysitron TI 950 nanoindenter with maximum applied load equal to 11 mN.

3. RESULTS AND DISCUSSION

Chemical composition of deposited TMSA coatings was determined using FTIR and XPS methods. **Figure 1** shows example of baseline-corrected IR absorbances normalized to the thickness of the film. All absorption peaks were identified according to the available literature [9,11-13]. IR spectra of TMSA coatings (**Figure 1**) showed significant absorption band from 1000 cm⁻¹ to ~1200 cm⁻¹ which is connected with Si-O-C/ Si-O-Si vibrations [9,11-13]. Structure of plasma polymers created using O₂ as a carrier gas are very similar to coatings based on siloxane chains (**Figure 1**) [9,11,13]. Intensities of these absorption peaks showed rapid increase with increasing ratio R , when oxygen was used as a carrier gas during deposition. Changes in intensities of Si-O-C vibrations were very low in case of thin films created from TMSA/Ar gaseous mixture, however usage of high amount of argon led to broadening of this peak towards lower wavenumbers and gradually went to the

region associated with silanol vibrations at $\sim 935\text{ cm}^{-1}$ (**Figure 1**) [12,13]. Medium absorptions presented at lower wavenumbers (spectral range from 750 cm^{-1} to 950 cm^{-1}) including peaks at 800 cm^{-1} , 840 cm^{-1} and 890 cm^{-1} are probably related to CH_3 rocking in $\text{Si}-\text{CH}_3$, to asymmetric stretching of $\text{Si}-\text{C}/\text{Si}-\text{O}$ bond and CH_3 rocking mode in $\text{Si}(\text{CH}_3)_{x=2,3}$ groups [11-13]. Deformation modes of $\text{Si}-\text{O}-\text{Si}$ may influence absorptions at 800 cm^{-1} and 890 cm^{-1} as well [12]. These structures gradually disappeared with increasing ratio of carrier gas (**Figure 1**).

Absorption peak at $\sim 1265\text{ cm}^{-1}$ was identified as deformation mode of CH_3 in $\text{Si}-\text{CH}_3$ group [11,12]. Content of $\text{Si}-\text{CH}_3$ in analyzed samples was confirmed by presence of absorption peaks typical for CH_3 stretching modes at 2880 cm^{-1} and 2960 cm^{-1} [11-13]. Symmetric and asymmetric stretching modes of CH_2 were determined in MIR spectra as well [11]. Since values of normalized absorbance in region of wavenumbers near 1400 cm^{-1} related to $\text{Si}-\text{CH}_2-\text{Si}$ [9] can be considered negligible, significant ratio of CH_2 groups probably formed long hydrocarbon chains. $\text{Si}-\text{CH}_3$ and hydrocarbon structures were more presented in plasma polymers formed in TMSA/Ar plasma in comparison with $\text{Si}-\text{O}-\text{C}$ (**Figure 1**) and their intensities showed decreasing trends with increasing R (ratio of carrier gas).

According to the IR spectra (**Figure 1**), TMSA-based plasma polymers contain $\text{C}=\text{O}$ functional groups characterized by absorption at 1720 cm^{-1} [9,11-13]. However, this peak had relatively low intensity in comparison with CH_x vibrations. Fraction of $\text{C}=\text{O}$ bonds in the structures of pp-TMSA decreased with increasing ratio R . If 75% of argon is used during deposition, intensity of $\text{C}=\text{O}$ vibration drops to the zero value and it is replaced by OH bending vibration associated with adsorbed water molecules (**Figure 1**) [13]. The absorption band spread in region above 3050 cm^{-1} is related to OH groups [11-13] presented in TMSA coatings. These stretching vibrations are connected with associated or isolated silanol groups and water molecules. OH stretching peaks were more significant in coatings formed in TMSA/ O_2 plasma. All investigated TMSA coatings include amount of hydrogen bonded to silicon which has characteristic peaks in region $2000\text{--}2450\text{ cm}^{-1}$ [13].

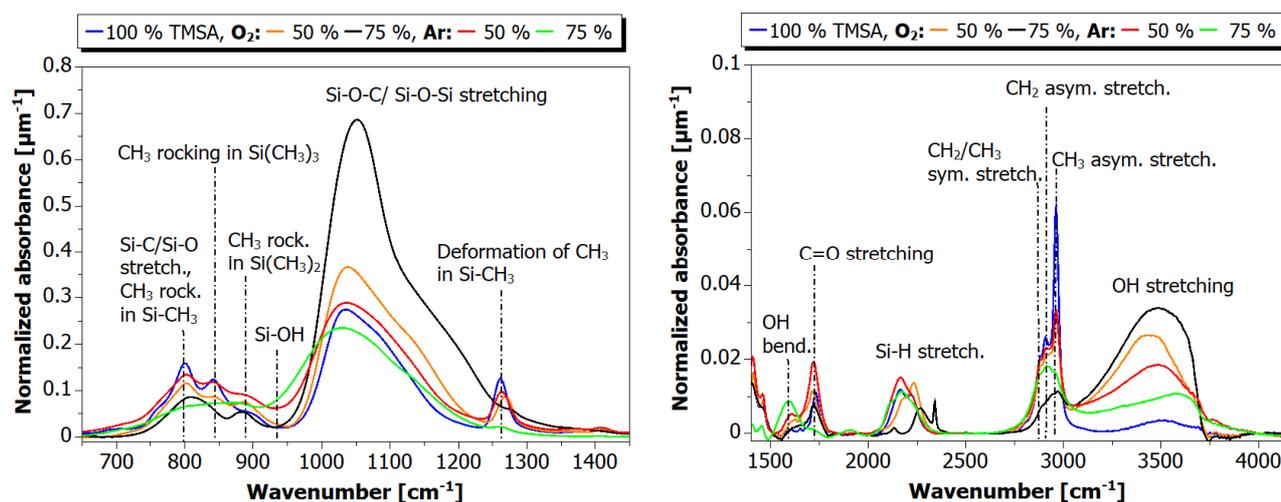


Figure 1 Examples of measured infrared spectra of TMSA plasma polymers

Surface chemistry of TMSA-based coatings was examined by XPS analysis. Characteristic peaks of silicon, carbon and oxygen atoms were detected at all studied surfaces. Results of atomic composition of TMSA-based surfaces are summarized in **Figures 2A-C**. Changes of atomic concentrations of carbon and oxygen (**Figures 2A, 2C**) presented at TMSA surfaces created using TMSA/Ar gaseous mixture were relatively low (less than 10 at. %) with increasing ratio R contrary to the films deposited from TMSA/ O_2 . Concentration of carbon showed decreasing trend with increasing amount of oxygen in gaseous mixture (**Figure 2A**). Atomic

concentration of oxygen significantly increased when higher amount of oxygen was used (**Figure 2C**). Concentration of silicon at TMSA surfaces formed in TMSA/O₂ slightly increased from 24 at. % to 31 at. % (**Figure 2B**). Number of silicon atoms for coatings prepared using argon as a carrier gas was ~21 at. % in range of *R* from 7 % to 50 %, then decrease at 5 at. % was observed (**Figure 2B**). Atomic concentration of Si at the surface deposited from 100 % of TMSA monomer was 10 at.%. The most of the surface carbon was bonded in $\underline{\text{C}}-\text{C}/\underline{\text{C}}-\text{H}$ chains (49-82 % of carbon). $\underline{\text{C}}=\text{O}$ functionalities were presented in negligible amounts: 0-4 % of carbon, as well as $\underline{\text{C}}-\text{Si}$. The rest of carbon atoms was presented in $\underline{\text{C}}-\text{O}$ bonds. According to the expectations [14], silicon atoms were part of $\underline{\text{Si}}(-\text{O})_{x=2,3,4}\text{C}_{y=2,1,0}$ structures. Formation of TMSA plasma polymer in TMSA/O₂ mixture using $R \geq 50\%$ led to the high concentrations of oxidized $\underline{\text{Si}}(-\text{O})_4$ structures (44 - 82 % of silicon). The rest of Si atoms was bonded in $\underline{\text{Si}}(-\text{O})_3\text{C}$ and $\underline{\text{Si}}(-\text{O})_2\text{C}_2$.

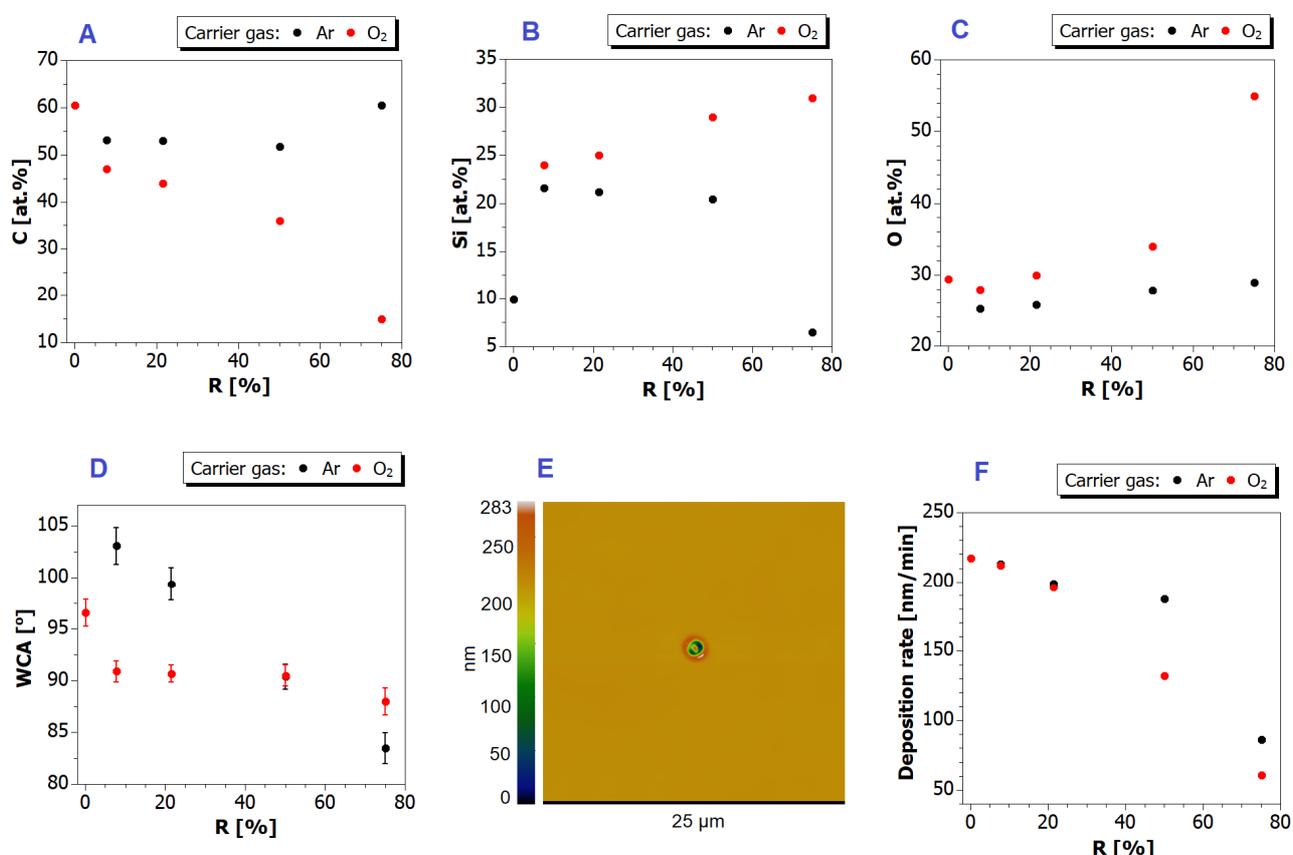


Figure 2 A: Atomic concentration of carbon on the surface in dependence on ratio of carrier gas used during deposition process; **B:** concentration of surface silicon; **C:** concentration of surface oxygen; **D:** dependence of measured water contact angle on *R*; **E:** Example of surface structure of thin film prepared from TMSA/Ar gaseous mixture using $R=50\%$; **F:** Graph of deposition rate in dependence on ratio *R*.

However, $\underline{\text{Si}}(-\text{O})_3\text{C}$ bonds, that showed decreasing concentration in dependence on ratio *R* (7 - 75 %) from 45 % of Si to 17 % Si, prevailed over $\underline{\text{Si}}(-\text{O})_2\text{C}_2$. Amount of $\underline{\text{Si}}(-\text{O})_2\text{C}_2$ structures decreased from 23 % of silicon atoms to zero with increasing *R* from 7 % to 75%. In case of thin films prepared in TMSA/Ar plasma, concentrations of $\underline{\text{Si}}(-\text{O})_4$ were negligible (0 - 4 % of Si) in comparison with less oxidized $\underline{\text{Si}}(-\text{O})_2\text{C}_2$ (53 - 63 % of Si) and $\underline{\text{Si}}(-\text{O})_3\text{C}$ structures (~37 % of Si). Concentration of $\underline{\text{Si}}(-\text{O})\text{C}_3$ was negligible for all studied TMSA coatings (~1 % of Si).

Figure 2D shows trends of measured water contact angle (WCA) in dependence on ratio of carrier gas *R*. Thin films prepared in TMSA/Ar discharge using $R < 50\%$ are hydrophobic (water contact angle is higher than 90°).

Dependence of WCA at the ratio R from 7 % to 75 % was decreasing from 103° to 84° (**Figure 2D**). Surfaces deposited from TMSA/O₂ plasma were considered hydrophilic: values of WCA were ~90° (**Figure 2D**).

Surface structure was examined by confocal microscopy. According to the results (**Figure 2E**), TMSA plasma polymers seems to be smooth with low number of defects. However, more detailed study of the surface microstructure using AFM technique is necessary for further discussion.

Indentation hardness H_{IT} and elastic modulus E_{eff} were examined using micro and nano indentation techniques. Values of indentation hardness increased with ratio R in range from 0 % to 75 % from 0.8 GPa to 7 GPa, when oxygen was used as a carrier gas. H_{IT} increased to 6 GPa in case of usage of TMSA/Ar mixtures. Values of elastic modulus E_{eff} increased from 15 GPa to 81 GPa for TMSA/O₂ coatings. Elastic modulus of TMSA/Ar thin films did not exceed 46 GPa.

Optical properties in UV/Visible spectral range were examined using ellipsometric measurements (Section 2). Fitting of available data allowed us to obtain approximate values of refractive index and extinction coefficient as well as thickness of resulting coatings. Refractive index of studied TMSA coatings, deposited using O₂ as a carrier gas, corresponding to the energy of 1.95 eV varied around 1.50, which is close to the refractive index of SiO₂ $n=1.47$. Refractive index of coatings prepared from TMSA/Ar increased from 1.6 to 1.7 with increasing R from 0 % to 50 %. The thin film created using 75 % of argon was photosensitive and unmeasurable in set spectral range (Section 2). Values of extinction coefficient for photon energy equal to 1.95~eV did not exceed $k=10^{-2}$ for all thin films characterized by UV/Visible ellipsometry.

According to the results summarized in this section, usage of oxygen during PECVD process leads to the formation of highly oxidized structures with higher amount of incorporated silicon resembling siloxane-based materials [1,2,9,14]. Higher wettability of surfaces created in TMSA/O₂ discharge is probably a consequence of observed oxygen incorporation. Differences in the growth mechanism of organosilicon coatings affect deposition rate as well as properties of resulting coatings. Trends of deposition rate, which is equal to the ratio of thickness of resulting film and deposition time, are shown in **Figure 2F**. Thickness of photosensitive coatings prepared using TMSA/Ar gaseous mixture with $R=75$ % was determined by profilometry (3D profilometer DektakXT Bruker). According to the **Figure 2F**, deposition rate decreases with increasing amount of carrier gas. If low ratio R (0 – 21 %) is used during PECVD process, deposition rates for argon and oxygen carrier gases can be considered equal. Deposition rate is higher if argon is used as a carrier gas for $R \geq 50$ %.

4. CONCLUSION

Properties of TMSA-based plasma polymers prepared in RF glow discharge using different carrier gases (O₂, Ar) were investigated by several characterization methods. Chemical structure of deposited coatings depends on choice of carrier gas as well as on ratio R of carrier gas in the mixture. The mechanical properties of studied TMSA-based coatings ranged from amorphous glass-like properties to properties of soft polymeric materials. The surface roughness of prepared coatings was very low, it was comparable with the roughness of the substrate surface. This work proves, that it is possible to prepare hydrophobic surfaces with relatively high amount of carbon bonded in $\underline{C}-C/\underline{C}-H$ chains using TMSA/Ar plasma. Therefore, our further research of coatings created using TMSA/Ar discharge will be oriented in this direction. Presence of carbonyl bonds at all examined surfaces was very low contrary to the $\underline{C}-C/\underline{C}-H$ and $\underline{C}-O$ bonds. Another part of future research will apply results presented in this study for optimization of production process of organosilicon coatings rich in C=O functionalities suitable for bioapplications.

ACKNOWLEDGEMENTS

This The present work was supported by Czech Science Foundation under project GACR 19-15240S, by Ministry of Education, Youth and Sports of the Czech Republic under project NPU (LO1411) and

by the project Brno Ph.D. Talent. Part of the work was carried out with the support of CEITEC Nano Research Infrastructure (ID LM2015041, MEYS CR, 2016-2019), CEITEC Brno University of Technology.

REFERENCES

- [1] ZAJÍČKOVÁ, L., BURŠÍKOVÁ, V., KUČEROVÁ, Z., FRANTA, D., DVOŘÁK, P., ŠMÍD, R., PEŘINA, V. and MACKOVÁ, A. Deposition of protective coatings in rf organosilicon discharges. *Plasma Sources Science and Technology*. 2007. vol. 16, no. 1, pp. S123-S132.
- [2] KO, Yeong-Mu, CHOE, Han-Cheol, JUNG, Sang-Chul and KIM, Byung-Hoon. Plasma deposition of a silicone-like layer for the corrosion protection of magnesium. *Progress in Organic Coatings*. 2013. vol 76, no. 12, pp. 1827-1832.
- [3] BURŠÍKOVÁ, V., SLÁDEK, P., ŠTAHEL, P., ZAJÍČKOVÁ, L. Improvement of the efficiency of the silicon solar cells by silicon incorporated diamond-like carbon antireflective coatings. *Journal of Non-Crystalline Solids*. 2002. vol. 299-302, no. 12, pp. 1147-1151.
- [4] CHOI, Yoo S., LEE, Joon S., JIN, Su B. and HAN, Jeon G. Super-hydrophobic coatings with nano-size roughness prepared with simple PECVD method, *Journal of Physics D: Applied Physics*. 2013. vol. 46, no. 31.
- [5] SHAHPANAH, Marjan, MEHRABIAN, Somayeh, ABBASI-FIROUZJAH, Marzieh and SHOKRI, Babak. Improving the oxygen barrier properties of PET polymer by radio frequency plasma-polymerized SiO_xN_y thin film, *Surface and Coatings Technology*. 2019. Vol. 358, pp. 91-97.
- [6] ELAGLI, Adil, BELHACENE, Kalim, VIVIEN, Céline, DHULSTER, Pascal, FROIDEVAUX, Renato, SUPIOT, Philippe. Facile immobilization of enzyme by entrapment using a plasma-deposited organosilicon thin film. *Journal of Molecular Catalysis B: Enzymatic*. 2014. vol. 110, pp. 77-86.
- [7] SARAPIROM, S., LEE, J. S., JIN, S. B., SONG, D. H., YU, L. D., HAN, J. G., CHAIWONG, C. Wettability effect of PECVD-SiO_x films on poly(lactic acid) induced by oxygen plasma on protein adsorption and cell attachment. *Journal of Physics: Conference Series*. 2013. vol. 423.
- [8] PRASAD, G. Ram, DANIELS, Stephen, CAMERON, D.C., MCNAMARA, B.P., TULLY, Elizabeth, O'KENNEDY, R. PECVD of biocompatible coatings on 316L stainless steel. *Surface and Coatings Technology*. 2005. vol. 200, no. 1-4, pp. 1031-1035.
- [9] BORVON, G., GOULLET, A., MELLHAOUI, X., CHARROUF, N., GRANIER, A. Electrical properties of low-dielectric-constant films prepared by PECVD in O₂/CH₄/HMDSO. *Materials Science in Semiconductor Processing*. 2003. vol 5, no. 2-3, pp. 279-284.
- [10] FRANTA, D., NEČAS, D., ZAJÍČKOVÁ, L. Models of dielectric response in disordered solids. *Optics Express*. 2007. vol. 15, no. 24, pp. 16230-16244.
- [11] CECH, V., ZEMEK, J., PERINA, V. Chemistry of Plasma-Polymerized Vinyltriethoxysilane Controlled by Deposition Conditions. *Plasma Processes and Polymers*. 2008. vol. 5, no. 8, pp. 745-752.
- [12] CASSERLY, T.B. and GLEASON K.K. Chemical Vapor Deposition of Organosilicon Thin Films from Methylmethoxysilanes. *Plasma Processes and Polymers*. 2005. vol. 2, no. 9, pp. 679-687.
- [13] GOULLET, A., VALLÉE, C., GRANIER, A. and TURBAN, G. Optical spectroscopic analyses of OH incorporation into SiO₂ films deposited from O₂/tetraethoxysilane plasmas. *Journal of Vacuum Science & Technology A: Vacuum Surfaces and Films*. 2000. vol. 18, no. 5.
- [14] GRÜNIGER, A., BIEDER, A., SONNENFELD, A., VON ROHR, Ph. Rudolf, MÜLLER, U., and HAUERT, R. Influence of film structure and composition on diffusion barrier performance of SiO_x thin films deposited by PECVD. *Surface and Coatings Technology*. 2006. vol. 200, no. 14-15, pp. 4564-4571.