ORGANOSILICON PLASMA POLYMERS BASED ON TRIMETHYLSILYL ACETATE MONOMER

Štěpánka KELAROVÁ, Vojtěch HOMOLA, Vilma BURŠÍKOVÁ

Department of Physical Electronics of Masaryk University, Brno, Czech Republic, EU
bittstep@gmail.com, vojhom@outlook.cz, vilmab@physics.muni.cz,

Abstract

Plasma-polymerized organosilicon coatings have been playing an important role in many research studies due to their wide range of applications. These materials can be used in industry as transparent wear resistant layers, protective hard a-Si:C:H or SiO2-like films, corrosion protection coatings, barrier films etc. Plasma-polymerization using organosilicon precursors has been investigated lately for development of unique thin film materials for bioapplications as well, including surface coating of surgical and dental implants to improve their biocompatibility. In the present work, low pressure RF capacitively coupled discharge was used to deposit thin solid films suitable for medical application from mixture of trimethylsilyl acetate (TMSA) and oxygen. Since resistance to liquid environment is the critical parameter that determines usability of the material for bioapplications, the deposited TMSA plasma polymers were exposed to water for 48 hours. The degree of stability varied with deposition parameters as well as other properties of organosilicon plasma polymers. This study summarizes changes of chemical structure and mechanical properties of resulting coatings in dependence on the ratio of TMSA and oxygen flow rates during the deposition process. Results of water stability tests included in present study proved that it is possible to prevent delamination of the coating during exposition to the aqueous environment by appropriate choice of discharge parameters.

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

1. INTRODUCTION

Thin solid films based on organosilicon monomer prepared by PECVD technology have been investigated intensively for many industrial applications such as corrosion protection coatings, transparent wear resistant layers, protective hard and antiscratch coatings for plastics, barrier films for pharmaceutical packaging etc. [1]. Organosilicon plasma polymers are very perspective for medical applications as well. It is possible to create organosilicon thin films suitable for protection of medical implants [2,3], organosilicon antibacterial coatings doped by silver nanoparticles [4] or materials enhancing osseointegration for dental implants [5]. Properties of plasma polymers (chemical composition, mechanical properties, stability in different environments etc.) are directly dependent on discharge parameters. These parameters (e.g. flow rates of the monomer and carrier gases, gas pressure, bias voltage etc.) can be varied to adapt resulting coatings for a particular purpose [1-7].

This study deals with characterization of organosilicon coatings deposited in RF glow discharge from gaseous trimethylsilyl acetate (TMSA) and oxygen. The aim of present work is to obtain water-resistant coatings suitable for bioapplications containing C=O functional groups which are presented in TMSA itself [8]. Changes in mechanical and chemical properties in dependence on the ratio of TMSA and O_2 flow rates were investigated as well as stability in water for 48 hours at 37 °C.

2. EXPERIMENTAL DETAILS

Organosilicon thin films were prepared in RF glow capacitively-coupled discharges at low pressures (20÷ 40 Pa) from mixture of TMSA ($CH_3CO_2Si(CH_3)_3$) and oxygen in a parallel plate reactor. The bottom electrode served as the substrate holder and it was coupled to RF generator (13.56 MHz) via a blocking capacitor. Silicon substrates were placed on the bottom electrode, the RF voltage of which was superimposed with a negative DC self-bias. The supplied power was kept at 50 W for all depositions and flow rates of TMSA and O_2 were changed. Changes of the flow rates are represented by the O_2 flow to TMSA flow rate ratio *R*.

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}. Thickness of each coating was measured using profilometer Bruker DektaXT immediately after deposition. Measurements of Martens hardness, elastic modulus and indentation hardness were realized using Fisherscope H100C microindentor. Stability of TMSA-based coatings in water for 48 hours at 37 °C was examined by observation of changes in surface structure using confocal laser microscope LEXT OLS4000 3D. The thickness loss caused by exposition to the liquid environment was determined by non-destructive ellipsometric method. All ellipsometric data were measured by Jobin Yvon UVISEL equipment at angle of incidence 65° in the spectral range from 1 eV to 5.5 eV. Thicknesses of plasma polymers were determined from fitting these data in program newAD by using PJDOS dispersion model [9]. Analyzed plasma polymers were immersed in liquid immediately after deposition.

3. RESULTS AND DISCUSSION

Chemical composition of TMSA plasma polymers was determined from baseline-corrected absorbance normalized to the thickness of the film in MIR spectral range (**Figure 1**) according to the available litarature [10-13]. Measured IR spectra (**Figure 1**) showed strong absorptions from 1035 cm^{-1} to ~1200 cm^{-1} in all studied TMSA-based thin films. These absorption peaks are related to the Si-O-C stretching vibrations in a continuous random network [10]. Structure of plasma polymers created using ratio of O_2/TMSA flow rates $R \geq 3$ is very similar to coatings based on siloxane chains [11-13]. Presence of Si-O-Si stretching vibrations typical for siloxane units [11-13] in this spectral range can not be excluded. However according to the chemical structure of TMSA monomer [8], Si−O−C presented in skeleton of original monomer are assumed to be predominant. Absorption peak at ~1265 cm^{-1} was identified as deformation mode of CH_3 in $Si-CH_3$ group [11,12]. 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 $Si-CH_3$, to asymmetric stretching of Si−C/Si−O bond and CH_3 rocking mode in $Si(CH_3)_{x=2,3}$ groups [11-13]. Deformation modes of Si−O−Si may influence absorptions at 800 cm^{-1} and 890 cm^{-1} as well [12]. Content of $Si-CH_3$ in analyzed samples was confirmed by presence of absorption peaks typical for CH_3 stretching modes at 2880 cm^{-1} and 2960 cm^{-1} [10-13]. Symmetric and asymmetric stretching modes of CH_2 were determined in MIR spectra as well [10-12]. Since values of normalized absorbance in region of wavenumbers near 1400 cm^{-1} related to $Si-CH_2-Si$ [11,13] can be considered negligible, significant amount of carbon is presumably bonded in hydrocarbon chains. According to the IR spectra (**Figure 1**), TMSA-based plasma polymers contain C=O functional groups characterized by absorption at 1720 cm^{-1} [10], however this peak has relatively low intensity in comparison with CH_x vibrations. All investigated TMSA coatings include amount of hydrogen bonded to silicon which has characteristic peaks in region 2000-2450 cm^{-1} [10,14]. The absorption band spread in region above 3050 cm^{-1} is related to OH groups [10-13].

Summarizing main trends observable in IR spectra, it is possible to conclude that amount of carbon bonded in $Si-CH_3$ and hydrocarbon chains significantly increased with decreasing ratio of O_2/TMSA flow rates *R* (increasing amount of TMSA monomer) used during deposition process. On the contrary, reaching the values of $R \geq 3$ amount of CH_x bonds rapidly decreased. Their absorptions were overlapped by spread peak of OH groups (**Figure 1**). These OH groups can be associated with silanols (other peaks at 920 cm^{-1} and 1190 cm^{-1}) [12] and partially bonded in adsorbed water molecules (OH stretching mode at ~3400 cm^{-1} and weak peak of bending mode at 1630 cm^{-1}) [11]. At the same time, absorptions in region from 1035 cm^{-1} to ~1200 cm^{-1}

related to Si−O−C/Si−O−Si network became more predominant (**Figure 1**). Changes in spectral region inluding Si-H bonds were observed as well: spread absorption around 2190 cm^{-1} transformed into narrow peak at 2343 cm^{-1} usually presented hexamethyldisiloxane coatings [14].

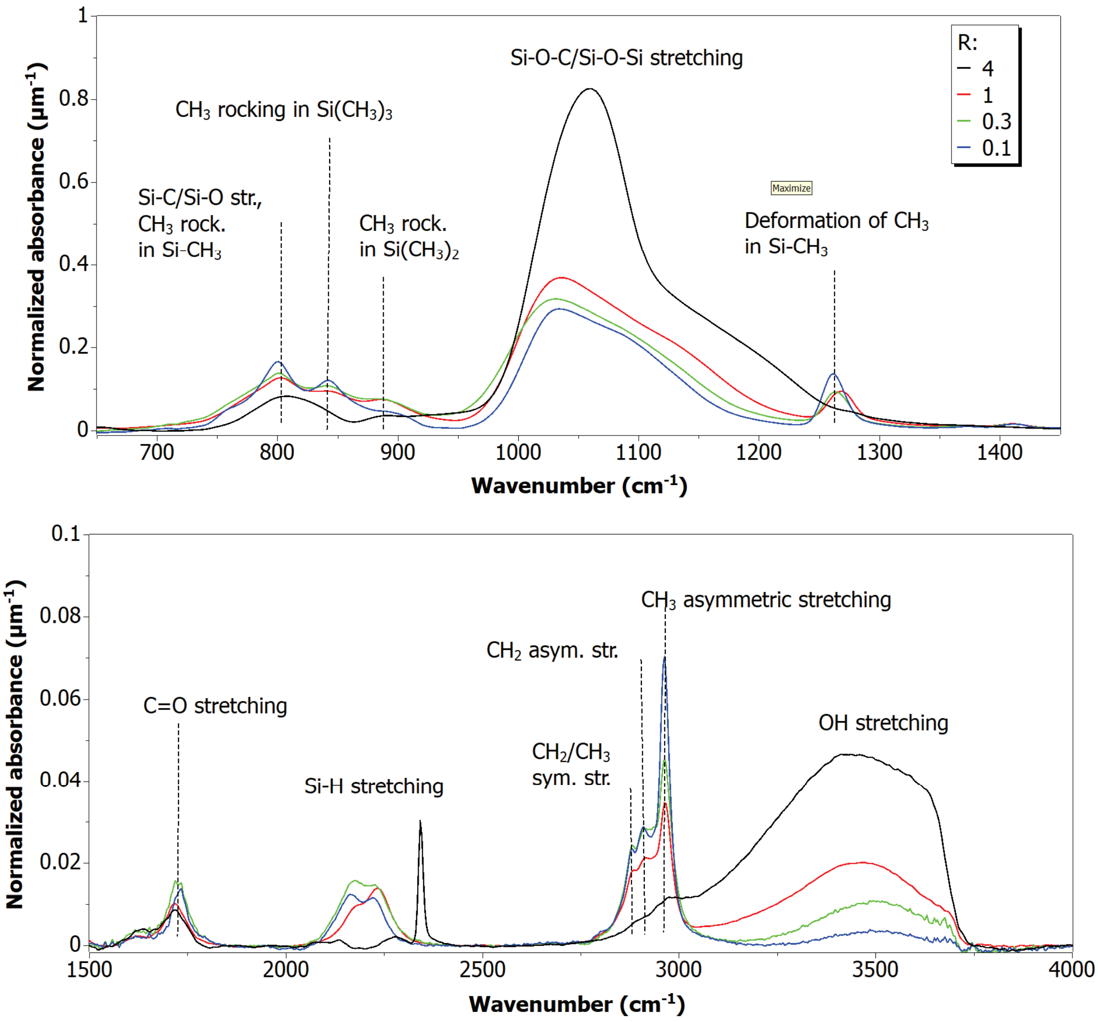

Figure 1 Infrared spectra of several TMSA plasma polymers prepared using different ratio *R* of O_2 and TMSA flow rates

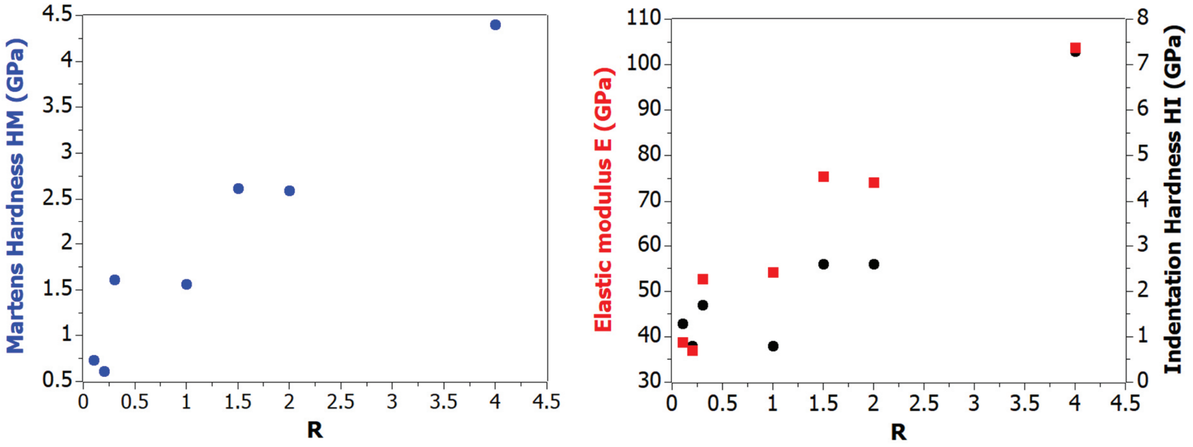

Figure 2 Mechanical properties of TMSA coatings in dependence on parameter *R*

Changes in chemical structure of deposited coatings described using IR spectroscopy had significant impact on mechanical properties of TMSA thin films. Trends of Martens hardness *HM*, elastic modulus *E* and indentation hardness *HI* in dependence on the parameter *R* are shown in **Figure 2**. All dependences shown in **Figure 2** have an increasing character with increasing ratio *R*.

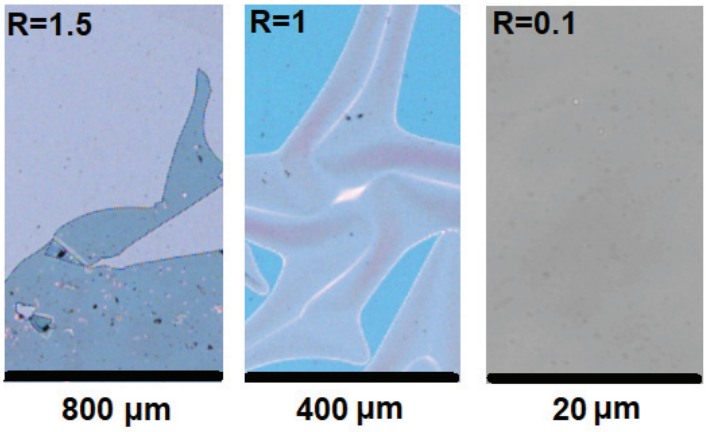

Figure 3 Pictures of chosen TMSA coatings after immersion in water taken by confocal microscope

The stability of TMSA-based plasma polymers in water for 48 h varied with parameter *R* as well as mechanical properties. Thin films prepared by using $R > 1$ were almost completely delaminated (**Figure 3**), while coatings deposited using high amount of TMSA ($R < 1$) were considered to be stable. Surfaces of these plasma polymers after immersion in water stayed smooth without defects and thickness losses determined by ellipsometry were at low values of ~3 %.

4. CONCLUSION

Properties of TMSA-based plasma polymers prepared in RF glow discharge were investigated by several characterization methods. Chemical structure of deposited coatings is directly linked to settings of flow rates of TMSA monomer and oxygen during deposition process. Changes in chemistry of plasma-polymerized TMSA influences mechanical properties and stability in water. Results of water stability tests included in present study proved that it is possible to prevent delamination of the coating during exposition to the aqueous environment by appropriate choice of TMSA and O_2 flow rates. Water-resistant TMSA coatings have a great potential for bioapplications, therefore our further research will be oriented in this direction.

ACKNOWLEDGEMENTS

This research has been supported by the project CZ.1.05/2.1.00/03.0086 funded by European Regional Development Fund and project LO1411 (NPU I) funded by MEYS of Czech Republic and by the project Brno Ph.D. Talent.

REFERENCES

[1] ZAJÍČKOVÁ, L., BURŠÍKOVÁ, V., KUČEROVÁ, Z., FRANCLOVÁ, J., SŤAHEL, P., PEŘINA, V., MACKOVÁ, A. Organosilicon thin films deposited by plasma enhanced CVD: Thermal changes of chemical structure and mechanical properties. *Journal of Physics and Chemistry of Solids.* 2007. vol. 68, no. 5-6, pp. 1255-1259

[2] VOGEL, K., WESTPHAL, N., SALZ, D., THIEL, K., WITTIG, L., CIACCHI, L.C., GRUNWALD, I. Dental implants coated with a durable and antibacterial film. *Surface Innovations*. 2015. vol. 3, no. 1, pp. 27-38

[3] BATORY, D., JEDRZEJCZAK, A., KACZOROWSKI, W., KOLODZIEJCZYK, L., BURNAT, B. The effect of Si incorporation on the corrosion resistance of a-C:H:SiOx coatings. *Diamond & Related Materials.* 2016. vol. 67, pp. 1-7

[4] SAULOU, C., DESPAX, B., RAYNAUD, P., ZANNA, S., SEYEUX, A., MARCUS, P., AUDINOT, J.N., MERCIER-BONIN, M. Plasma-Mediated Nanosilver-Organosilicon Composite Films Deposited on Stainless Steel: Synthesis, Surface Characterization, and Evaluation of Anti-Adhesive and Anti-Microbial Properties on the Model Yeast Saccharomyces cerevisiae. *Plasma Process. Polym.* 2012. vol. 9, no. 3, pp. 324-338

[5] HYAKAWA, T., YOSHINARI, M., NEMOTO, K. Characterization and protein-adsorption behavior of deposited organic thin film onto titanium by plasma polymerization with hexamethyldisiloxane. *Biomaterials.* 2004. vol. 25, no. 1, pp. 119-127

[6] WRÓBEL, A. Aging process in plasma-polymerized organosilicon thin films. *Journal of Macromolecular Science: Part A - Chemistry.* 1985. vol. 22, no. 8, pp. 1089-1100

[7] BLANCHARD, N.E., NAIK, V. V., GEUE, T., KAHLE, O., HEGEMANN, D., HEUBERGER, M. Response of plasma-polymerized hexamethyldisiloxane films to aqueous environments. *Langmuir.* 2015. vol 31, no. 47, pp. 12944-12953

[8] BALL, I.K., HARRISON, P.G., TORR, A. FTIR study of thermally induced transformations of trimethylsilylmethyl acetate in the temperature range 623-813 K. *Journal of Organometallic Chemistry*. 2000. vol. 599, no. 2, pp. 185-194

[9] FRANTA, D., NEČAS, D., ZAJÍČKOVÁ, L. Models of dielectric response in disordered solids. *Optics Express.* 2007. vol. 15, no. 24, pp. 16230-16244

[10] CECH, V., ZEMEK, J., PERINA, V. Chemistry of Plasma-Polymerized Vinyltriethoxysilane Controlled by Deposition Conditions. *Plasma Process. Polym*. 2008. vol. 5, no. 8, pp. 745-752

[11] TSANKOV, D., RADEVA, E., HINRICHS, K., RÖSELER, A., KORTE, E.H. Infrared spectroscopic ellipsometry and atomic force microscopy study of plasma polymerized hexamethyldisiloxane layers post-treated by NH3 plasma. *Thin solid films.* 2005. vol. 476, no. 1, pp. 174-180

[12] CASSERLY, T.B., GLEASON K.K. Chemical Vapor Deposition of Organosilicon Thin Films from Methylmethoxysilanes. *Plasma Process. Polym.* 2005. vol. 2, no. 9, pp. 679-687

[13] Borvon, G., Goullet, A., Mellhaoui, X., Charrouf, N., Granier, A. Electrical properties of low-dielectric-constant films prepared by PECVD in O_2/CH_4/HMDSO. *Materials Science in Semiconductor Processing.* 2003. vol 5, no. 2-3, pp. 279-284

[14] MURESAN, M.G., CHARVÁTOVÁ CAMPBELL, A., ONDRAČKA, P., BURŠÍKOVÁ, V., PEŘINA, V., POLCAR, T., REUTER, S., HAMMER, M.U., VALTR, M., ZAJÍČKOVÁ, L. Protective double-layer coatings prepared by plasma enhanced chemical vapor deposition on tool steel. *Surface & Coatings Technology*. 2015. vol. 272, pp. 229-238