

## STUDY OF NITROGEN DOPED ORGANOSILICON PLASMA POLYMER THIN FILMS

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### Abstract

Plasma polymerized hexamethyldisiloxane coatings have been attracting interest of many researches. Due to their properties, these materials have a great potential to succeed in large field of applications such as protective anti-scratch layers on plastic substrates, corrosion protection coatings, barrier films for pharmaceutical packaging etc. Functionalized organosilicon plasma polymers have been investigated for development of unique biomaterials. Addition of a suitable dopant during plasma polymerization is one of the ways to form specific functionalities modulating chemistry, physical properties as well as biocompatibility of the films. In the present work, low pressure RF capacitively coupled discharge was used to deposit organosilicon thin films with nitrogen-containing functional groups on single crystalline silicon substrates. Resulting plasma polymers were investigated by several methods aimed primarily at determination of chemical composition, surface microstructure and mechanical properties. The present study includes results of Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, confocal microscopy, atomic force microscopy and nanoindentation, and their comparison with respect to deposition parameters.

**Keywords:** Thin films, hexamethyldisiloxane, PECVD, FTIR, XPS, AFM, nanoindentation

### 1. INTRODUCTION

Hexamethyldisiloxane (HMDSO) - based coatings have been investigated these days by many scientific groups. Due to their properties, these materials have a great potential to succeed in large field of industrial applications such as protective anti-scratch layers on plastic substrates, corrosion protection coatings, barrier films for pharmaceutical packaging etc. [1]. Plasma polymerized HMDSO (ppHMDSO) has been studied for several applications in medicine. These types of layers were investigated for possible usage as a protective coatings for medical implants [2], [3]. They were also successfully applied onto magnetic nanoparticles that are very perspective for medical applications [4], [5]. For example, it is possible to create super-hydrophilic surface by plasma polymerization of HMDSO [6], which prevents the aggregation of the particle cores in organic solvents [7].

By means of doping of variety of elements, it is possible to influence plenty of factors of HMDSO-based thin films, like mechanical properties, conductivity, surface free energy, biocompatibility etc. It was proved, that the nitrogen content in diamond-like carbon (DLC) or silicon-nitride HMDSO coatings strongly influences mechanical properties of the films. By addition of nitrogen or ammonia during plasma enhanced chemical vapor deposition (PECVD) process it is possible to adjust coatings hardness, elastic modulus or fracture toughness for desired industrial application [8], [9].

HMDSO-based organosilicon plasma polymers with amount of amine functional groups on the surface can find wide application in various fields of biochemistry, biology and medicine. Functionalization of organosilicon materials is commonly achieved by plasma treatment in nitrogen or ammonia [10], [11], or by deposition of functionalized coating on organosilicon surface [12]. Organosilicon plasma polymer with a content of amine functional groups can be deposited from gaseous monomer containing these functionalities [13], or by addition of suitable dopant to organosilicon monomer during PECVD process [14].

This study deals with properties of nitrogen-doped pp-HMDSO in dependence on parameters of PECVD process, that were originally developed and investigated as protective coatings for polymer substrates, and discusses their possible usage for bioapplications.

## 2. EXPERIMENTAL DETAILS

Thin films were prepared in RF capacitive discharges at low pressures ( $10 \div 30$  Pa) from mixture of HMDSO ( $\text{SiO}_2\text{C}_6\text{H}_{18}$ ) and nitrogen 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. Double-side polished 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 HMDSO and nitrogen were changed. Changes of the flow rates are represented by the ratio  $R$  of nitrogen flow rate and HMDSO flow rate.

Properties of the prepared films were studied by several characterization methods. Chemical composition of the resulting coatings was investigated by Fourier transform infrared spectroscopy (FTIR) using spectrometer Bruker Vertex 80v, in range from  $370\text{ cm}^{-1}$  to  $7500\text{ cm}^{-1}$  with 500 scans and resolution  $8\text{ cm}^{-1}$ . All manipulations of measured absorption spectra were performed by using OPUS program. Other optical method used for study of deposited layers was ellipsometry in UV and visible region. All ellipsometric data were measured by Jobin Yvon UVISEL equipment at three angles of incidence  $55^\circ$ ,  $65^\circ$  and  $75^\circ$ , in the spectral region of 240-800 nm. Thicknesses of plasma polymers were determined from fitting resulting data in program newAD by using PJDOS dispersion model [15].

Surface chemical composition was investigated by X-ray photoelectron spectroscopy (XPS). The XPS measurements were done on the ESCALAB 250Xi (ThermoFisher Scientific). The system is equipped with 500 mm Rowland circle monochromator with microfocused Al K $\alpha$  X-Ray source. An X-ray beam with 200 W power (650 microns spot size) was used. The XPS analysis was performed on surfaces under Ar<sup>+</sup> ion bombardment cleaning (3 keV ion energy, sputtering time 5 minutes). The survey spectra were acquired with pass energy of 50 eV and resolution of 1 eV. High-resolution scans were acquired with pass energy of 20 eV and resolution of 0.1 eV. In order to compensate the charges on the surface electron flood gun was used. Spectra were referenced to the hydrocarbon type C 1s component set at a binding energy of 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software.

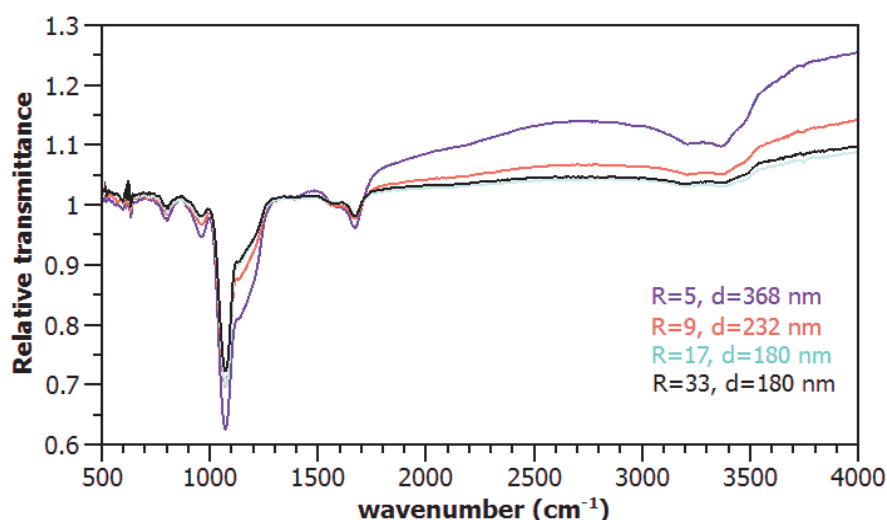
Surface microstructure was observed by confocal laser microscope LEXT OLS4000 3D and then in more detail by atomic force microscope Ntegra Prima NT-MDT in semicontact mode. Surface parameters were investigated in Nova Px program.

Nanoindentation data were obtained using Hysitron TI950 nanotriboindenter equipped with diamond Berkovich tip. The quasistatic loading curves with 20 unloading segments were applied in the load region from 200 to 11000  $\mu\text{N}$  to study the depth profile of the hardness and elastic modulus of the coating/substrate systems.

## 3. RESULTS AND DISCUSSION

The chemical composition of the films was investigated by combination of two available characterization methods: FTIR and XPS. The transmittance measured in IR region is influenced by both, the specific plasma polymer and the silicon substrate. The substrate influence was eliminated dividing the composite signal by the transmittance of the substrate used. The resulting relative transmittance (**Figure 1**) was then analyzed according to the available literature. Significant absorptions corresponding to the Si-O-Si vibrations at  $800\text{ cm}^{-1}$  and  $1066\text{ cm}^{-1}$  were observed in all of analyzed HMDSO-based coatings (**Figure 1**) [16]. The peak at  $960\text{ cm}^{-1}$  was assigned to the Si-N bond [17], while the absorption region between  $1100$  and  $1250\text{ cm}^{-1}$  includes three types of organic bonds: SiOC, CO, CN [14], [18]. Absorption regions shown in **Figure 1** around  $1600\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$  connected with specific functionalities are problematic for interpretation. The peak at the position of  $1570\text{ cm}^{-1}$  identified as NH bending vibration is common for amide (NC=O) compounds as well

as C=O vibration at  $\sim 1660\text{ cm}^{-1}$  [19]. However, absorption band of C=O overlaps with  $\text{NH}_2$  scissoring signal of primary amines. The presence of primary amines cannot be disproved according to the IR spectroscopy, because the region of relative transmittance between  $3000\text{ cm}^{-1}$  and  $3550\text{ cm}^{-1}$  includes NH stretching of primary amines, secondary amines and amides. In addition, it is common to observe in spectra of primary amines significant absorption in the range of frequencies  $3150\text{--}3250\text{ cm}^{-1}$ , which is attributed to the first overtone of  $\text{NH}_2$  scissoring [20]. NH stretching absorption peaks overlap with OH stretching vibration. Since the studied plasma polymers were exposed to the atmosphere before FTIR measurement, they probably include significant amount of adsorbed water, which is represented by OH absorption approximately at  $3400\text{ cm}^{-1}$  (stretching vib.) and  $1600\text{ cm}^{-1}$  (bending vib.) [21].



**Figure 1** Examples of IR spectra for selected ratios  $R$  of flow rates of nitrogen and HMDSO

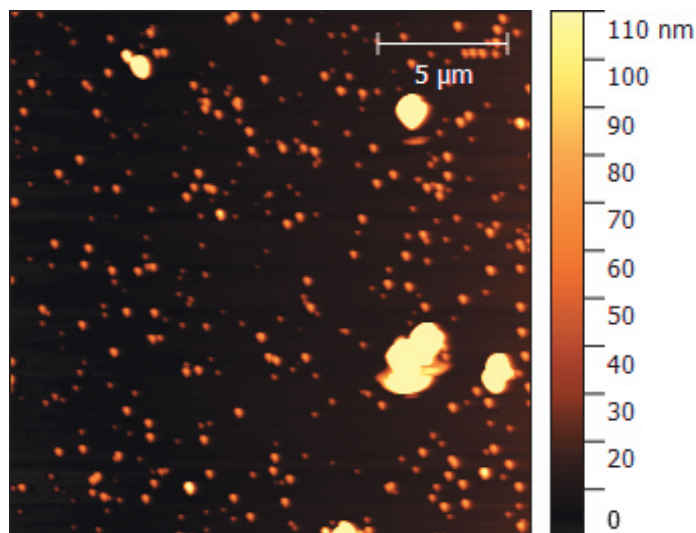
The XPS study of surface chemistry showed presence of four elements: Si, O, C, N listed in **Table 1**. Oxygen is the most abundant element on surfaces of analyzed organosilicon polymers. Its atomic concentration varies between 49–60 at. % in dependence on ratio  $R$  of gaseous mixture (**Table 1**). Plasma polymers with maximum quantity of oxygen consist of minimum amount of nitrogen and carbon (**Table 1**). Atomic concentration of silicon varies around  $\sim 35$  at. %. The high amount of oxygen possibly arises from the high amount of adsorbed water, which was found in absorption peaks in measured IR spectra around  $1600\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ , which are mostly created by OH vibrations.

**Table 1** Results of XPS analysis of the surface including atomic concentrations of elements and chemical bonds

$R$	N (at.%)	C-NH <sub>2</sub> (at.%)	SiNO <sub>2</sub> (at.%)	NSi <sub>3</sub> (at.%)	C (at.%)	C=O (at.%)	Si (at.%)	Si <sup>2+</sup> (at.%)	Si <sup>4+</sup> (at.%)	Si <sub>3</sub> N <sub>4</sub> (at.%)	O (at.%)
3	4.6	1.7	1.3	1.6	9.9	3.1	33	17	17	5	49
5	4.9	0.4	0	4.6	8.5	0.6	32	4	24	4	54
9	4.0	0.5	0.9	2.6	5.9	0.7	35	5	23	7	55
14	3.0	0.7	0.2	2.1	4.5	0.3	34	9	23	2	55
17	1.7	0.1	0	1.6	2.5	0.2	35	1	28	7	60
21	1.6	1.5	0	0.1	2.2	0.1	36	2	31	3	60
33	3.8	2.0	0	1.8	5.3	0.5	35	6	22	6	55

The complete functional composition of measured layers was derived from the fitting of Si2p, C1s and N1s XPS signals. Individual components of the fits were identified according to the available literature [16], [22]. In this text, we will concentrate on content of functionalities, which are interesting for bioapplications. Unfortunately, the results of fitting of N1s signal show, that the majority of nitrogen is bonded to silicon atoms in silicon nitride ( $\text{N}_2\text{Si}_3$ ) and  $\text{SiNO}_2$ . Atomic concentration of C-NH<sub>2</sub> is negligible (**Table 1**). However, ratio of flow rates of HMDSO and nitrogen  $R$  influences the concentrations of C-NH<sub>2</sub> and  $\text{N}_2\text{Si}_3$  in N1s environment as well as elemental composition. According to the **Table 1**, atomic concentration of surface nitrogen and C-NH<sub>2</sub> reach the minimum at about  $R=17$  and then there is an increase. For possible applications in biological and medical fields it will be advantageous to investigate wider range of  $R>17$  and find limit for increase in the proportion of nitrogen and amine groups on the surface. C1s signal includes six compounds in sum: Si-C, C-C, C-N, C-O/COH, C=O (aldehydes, ketones, amides) and OCO (acetal). Atomic concentration of C=O groups, that belong together with amines to functionalities suitable for immobilization of biomolecules and cell cultivation [23], listed in **Table 1** is similar to amine amount. In order to investigate the nature of silicon environment the Si2p peak was fitted with a sum of three contributions: silicon bonded to two oxygens ( $\text{Si}^{2+}$ ), silicon with four bonds to oxygen ( $\text{Si}^{4+}$ ) and silicon coordinated in silicon nitride ( $\text{Si}_3\text{N}_4$ ). The  $\text{Si}^{2+}$  corresponds to the initial structure of silicon in HMDSO, while  $\text{Si}^{4+}$  corresponds to inorganic silicon oxide. Silicon environment is formed mainly by inorganic compounds, however it is possible to influence character of the surface by optimization of deposition parameters (**Table 1**).

Two different techniques were used for observation of surface microstructure: confocal microscopy and AFM. HMDSO plasma polymers can be considered as smooth with number of nanoparticles, which are spread over the observed area (**Figure 2**). The film hardness and elastic T modulus decreased with  $R$  from 9 to 0.7 GPa and from 65 to 18 GPa, respectively. However, this decrease was mostly caused by the decrease of the bias voltage with increasing  $R$ .



**Figure 2** Example of surface microstructure of doped pp-HMDSO investigated by AFM for  $R=21$

#### 4. CONCLUSION

Organosilicon thin films with nitrogen-containing functional groups were deposited using RF glow discharges. The films were investigated by several methods aimed primarily at determination of chemical composition, surface microstructure and mechanical properties. The FTIR and XPS analyses revealed inorganic/ organic nature of plasma polymers. Surfaces of investigated pp-HMDSO are poor for amine functionalities and because of this reason they are not suitable for immobilization of biomolecules, however they could be potentially applied as an interlayers between substrate and functionalized coatings.

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