ENVIRONMENTAL STABILITY OF NITROGEN CONTAINING PLASMA-POLYMERIZED HEXAMETHYLDISILOXANE FILMS

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Abstract

Nitrogen incorporated organosilicon films were prepared by means of plasma enhanced chemical vapor deposition using capacitively coupled RF glow discharges in mixtures of hexamethyldisiloxane and nitrogen. The flow rate of nitrogen was 2-10 sccm and the flow rate of hexamethyldisiloxane was 0.3-0.4 sccm. The power supply of CCP was 50 W.

The environmental stability of the deposited films was studied using confocal microscopy, spectroscopic ellipsometry and FTIR (Fourier Transform Infrared Spectroscopy). The humidity induced structure changes resulted in substantial change of mechanical properties of the studied films. The mechanical properties were studied using nanoindentation techniques.

Keywords: Plasma polymer films, plasma enhanced chemical vapor deposition, FTIR, nanoindentation

1. INTRODUCTION

Organosilicon plasma polymers deposited from hexamethyldisiloxane (HMDSO) monomer hold the prospect of combining many advantageous properties for broad field of applications. They have a great potential for industrial use as a protective anti-scratch layers, corrosion protection coatings, protective coatings on optical devices, permselective membranes and barrier films etc, as well as in biomedical applications [1-8].

In the present work, we study thin films prepared from mixture of hexamethyldisiloxane and nitrogen in radiofrequency glow discharge. The growing mechanisms of the plasma polymer coatings and the way how the plasma polymer film structure is influenced with the deposition process parameters was investigated. The main focus was on the study of the films environmental stability, what plays a crucial role in their application. The environmental stability of the deposited films was studied using confocal microscopy, spectroscopic ellipsometry and FTIR (Fourier Transform Infrared Spectroscopy). Moreover, the humidity induced structure changes on mechanical properties of deposited films was studied using nanoindentation techniques.

2. EXPERIMENTAL

The studied thin films were prepared in radiofrequency glow discharges at low pressures (10 ÷ 30 Pa) from mixture of HMDSO ($SiO_2C_6H_{18}$) and nitrogen in a capacitively coupled parallel plate reactor [4]. 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.

The chemical composition of the deposited films 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 8 cm^{-1}. Measured IR spectra (transmittance of thin film and silicon substrate) were divided by transmittance of used substrate. Resulting relative transmittance was converted to absorbance. These data

were modified by cubic spline baseline correction. Moreover, the films optical properties were studied using ellipsometry in UV and visible region. All ellipsometric data were measured by Jobin Yvon UVISEL equipment at tree angles of incidence 55 °, 65 ° and 75 °, 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 [10].

The humidity induced changes in film surface topography were observed by confocal laser microscope LEXT OLS4000 and then in more detail by atomic force microscope NTEGRA PRIMA.

The hardness H and effective elastic modulus E_{eff} (E_{eff} = E/(1-ν^2), where E is the Young's modulus and ν is the Poisson's ratio of the tested material) were measured and evaluated by indentation techniques performed using Hysitron TI950 Triboindenter and Fischerscope H100 testers, both equipped with Berkovich tips. In case of nanoindentation the tip diameter was less than 50nm. The standard procedure proposed by Oliver and Pharr [9] was used for the evaluation of the hardness and elastic modulus from quasistatic tests. The load resolution was around 1 nN and the load noise floor less than 30 nN. Nanodynamic mechanical analysis (nanoDMA) was used in the range of indentation loads from 0.01 to 11 mN. The load oscillation frequency was 220 Hz and its amplitude ranged from 0.5 to 2.5 nm. The nanodynamical analysis was carried out in the linear loading rate regime. The pre-load of 0.5 µN was set to ensure good contact between the tip.

Moreover, several quasistatic indentation test were performed by Fisherscope H100 instrumented indentation tester in the load range from 10 to 100 mN and the Martens Hardness was studied. The Martens hardness value is calculated by dividing the maximum applied load by the surface area of the indenter penetrating beyond the original surface of the tested material. The applied load of 100 mN was used in order to study the differential hardness H_{diff} and the resistance of the coating/substrate system against delamination. Berkovich indenter with tip radius of 200nm was used for this tests. The load increase was controlled according to function $L=Ct^2$, where L is the load, t is the time and the constant C=25mNs^{-2}. The differential hardness was calculated as the derivative of the indentation load according to the contact area. The differential hardness dependence on the indentation depth was used to visualize the defect creation in the tested materials.

3.   RESULTS

The presented work builds on previous results presented in the proceedings of the Conference Nanocon 2016 [4]. In the previous work we studied the dependece of chemical composition and physical properties of nitrogen doped PPHMDSO films on the nitrogen to HMDSO flow rate ratio *R* in a relatively wide range from 3 to 33.

For the present work we selected 3 samples with different *R* (5, 17, 33) prepared under the conditions described in the previous work in order to study the reproducibility of the deposition process as well as the environmental stability of the deposited thin films. The deposition conditions are given in **Table 1**. The results obtained using FTIR studies on the selected samples are illustrated in **Figure 1**.

Table 1 Summary of deposition conditions together with deposition rates obtained from ellipsometric results. Q_N is the nitrogen and Q_{HMDSO} is the HMDSO flow rate, *R* is the ratio of flow rates and Ub is the DC bias voltage at the beginning and at the end of deposition process

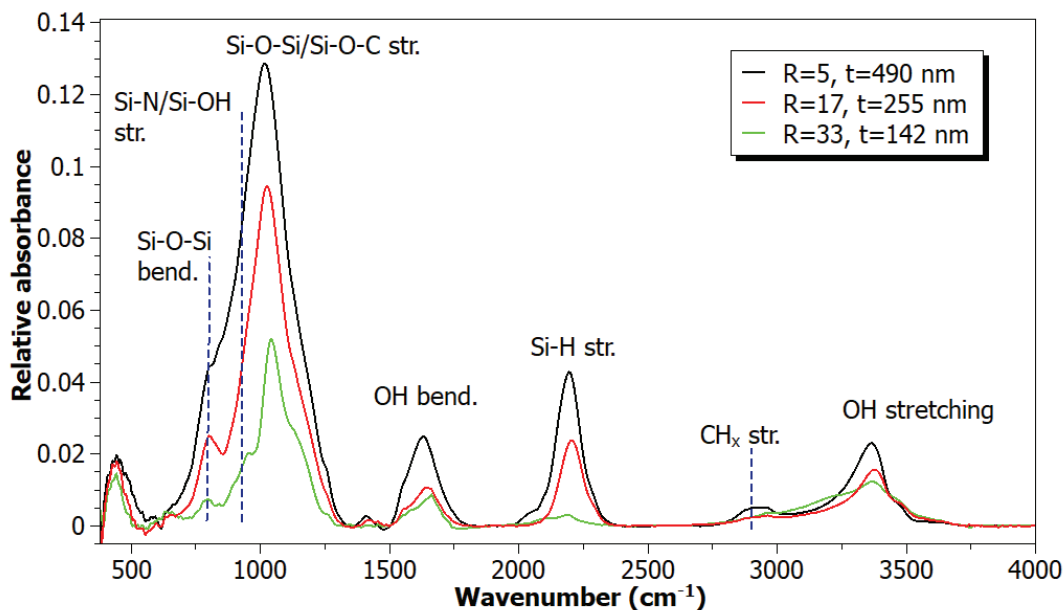| Sample	Q_N [sccm]	Q_{HMDSO} [sccm]	*R*	U_b [V]	Dep. rate [nm/min]
1	2	0.4	5	-320/-360	40.8
2	5	0.3	17	-215/-246	15.5
3	10	0.3	33	-80/-125	14.2

Figure 1 IR spectra of the as-deposited films

The absorption peaks centered around 450 cm^{-1} may be associated with Si-O-Si rocking [11] and/or Si_3N stretching [12]. Significant absorptions were observed in the MIR region from 800 cm^{-1} to 1250 cm^{-1} for all three studied films (**Figure 1**). There are several characteristic vibrations around 800 cm^{-1} in IR spectra of organosilicon films including Si-O-Si bending at 800 cm^{-1}, CH_3 rocking in $Si(CH_3)_n$ (835 cm^{-1}) and Si-N stretching at 850 cm^{-1} [13,14,15]. Spectral range from 950 cm^{-1} to 1200 cm^{-1} include absorption peaks of Si-O-R chains (Si-O-Si asymmetric stretch: 1036 and 1060 cm^{-1}, Si-O-C stretching vibrations at 965 cm^{-1} and 1160 cm^{-1}) [13,15,16]. Absorption signal around 1230 cm^{-1} is probably a result of CH_3 wagging of $Si-CH_3$ group [13]. Si-O-C vibrations at 965 cm^{-1} are possibly partially overlapped by absorption peaks of Si-OH (~920 cm^{-1}) and by Si-N stretching at ~930 cm^{-1} typical for nitrogen containing organosilicon films [14,17]. In **Figure 1**, there is a strong absorption centered around 2170 cm^{-1}, which can be assigned to Si-H valence vibration [16]. The region from 2850 to 2960 cm^{-1} is characteristic for asymmetric and symmetric stretching of CH_3 and CH_2 groups [13,16]. Studied HMDSO-based plasma polymers include significant amount of adsorbed water, which is represented by broad OH stretching peak approximately at 3400 cm^{-1} and OH bending vibration at 1600 cm^{-1} [13,16].

The above described samples were used to study their aging under laboratory conditions. All studied layers have lost hydrogen in the Si-H bonds within a few days of aging. The rate of Si-H decay differed for each sample. This difference can be due to both the different chemical composition of individual layers and their different thicknesses.

In case of the sample with *R*=5, 490 nm thick, Si-H bonds vanished within 48 hours, what was accompanied with film thickness increase to 600 nm and RMS (Rooth Mean Square) roughness from 0.3 nm to 0.6 nm.

In case of sample with *R*=17 and thickness *t*=255 nm, the Si-H bonds vanished within 24 hours, however the sample thickness change was very small even after 48 hours (increase of 18 nm), which is almost in the frame of the experimental error (±6 nm) of the thickness determination. The RMS roughness (0.7 nm) of this film remained the same in the frame of the experimental error of roughness evaluation.

Sample with *R*=33 and *t*=142 nm did not contain Si-H bonds at all. It is possible both, either the as-deposited layer did not contain Si-H bonds or the Si-H bonds decay occurred in an extremely short time. RMS roughness increased from 1.2 to 1.5 nm.

In case of samples with R=5 and 17 there were observed significant changes in the spectra also in the region of the wave lengths from 700 to 1300 cm^{-1}.
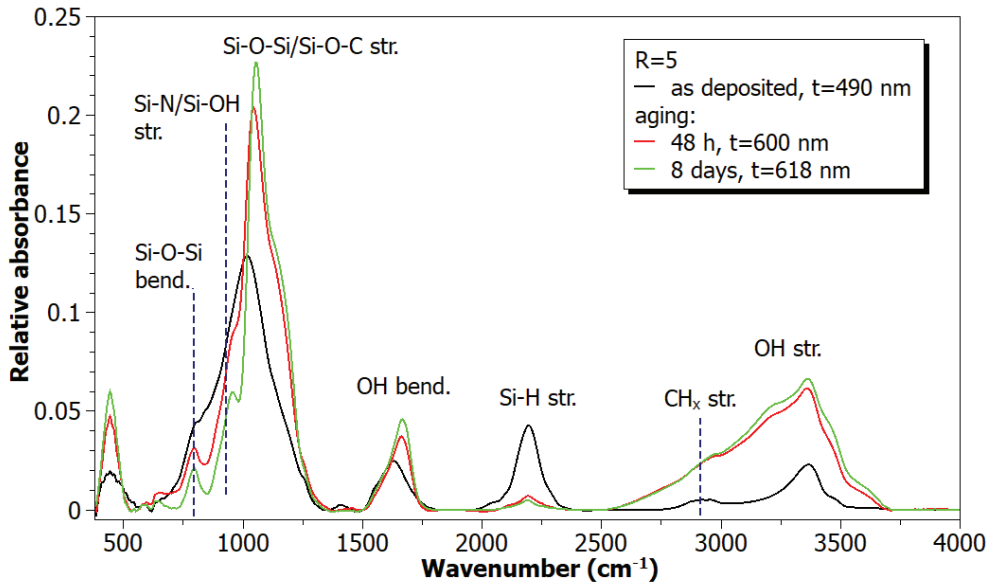

Figure 2 IR spectra of sample with R=5. Comparison of the as-deposited state with spectra acquired after several times of aging on air under laboratory conditions

An example of the humidity induced structure changes is illustrated in **Figure 2.**, where the IR spectra acquired on sample with R=5 are shown after several different times of sample aging on air under laboratory conditions. It is evident from the **Figure 2**, that in addition to the reduction of Si-H bonds, the number of OH, Si-O-Si and Si-O-C groups have been increased. Similar trends were described in [18] for plasma polymers prepared from methylsilane, methylsilazane, and methylsiloxane precursors. The diffusion of atmospheric oxygen and water into the as-deposited films caused substantial decrease in the hardness and elastic modulus of the samples mainly due to the increase of the number OH groups in the films (see **Figure 3a**). Moreover, the film volume increase resulted in increase of compressive stress and the films became less resistant against indentation induced delamination. The results of nanoDMA measurements in **Figure 3b** illustrate the non-homogeneous hardness and elastic modulus depth profiles of films after aging.
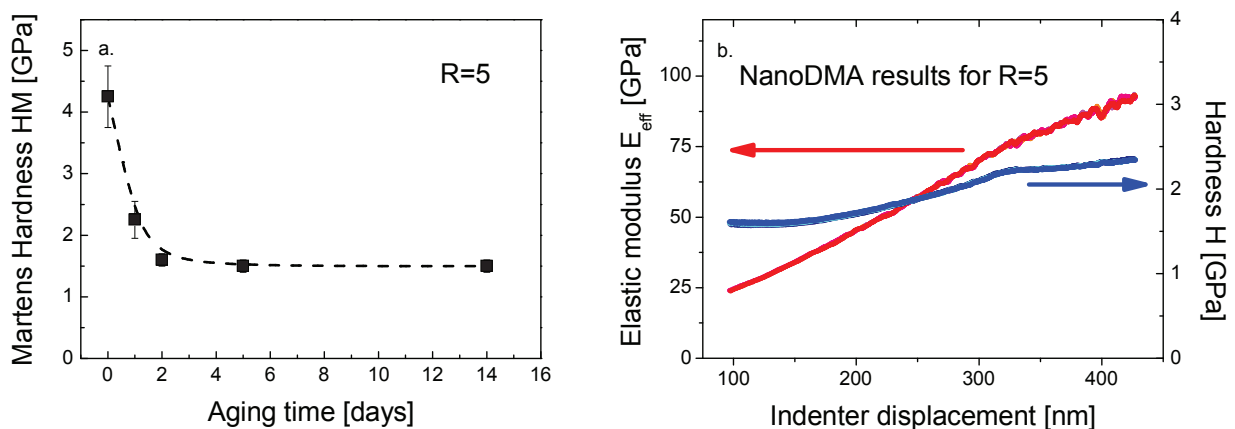

Figure 3 Example of the dependence of the Martens Hardness on the aging time measured with applied load of 10mN (a.) and the dependence of the effective elastic modulus and indentation hardness on the indenter displacement measured after aging (b.) for sample R=5

CONCLUSION

The process of aging in nitrogen doped plasma-polymerized organosilicon thin films was studied at laboratory conditions. The IR spectroscopic results revealed significant influence of aging on the films structure. The decay of Si-H groups and the increase of OH related bonds were found to be the most dominant processes in the structural changes resulting from aging at air. The structural changes were accompanied by substantial changes in film thickness. These changes occur because of the diffusion of atmospheric oxygen and water into the as-deposited films.

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