DEVELOPMENT OF PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION REACTOR FOR PREPARATION OF OXYGEN CONTAINING ORGANOSILAZANE POLYMER THIN FILMS

Roman PŘIBYL, Štěpánka KELAROVÁ, Vojtěch HOMOLA, Vilma BURŠÍKOVÁ

[1]Department of Physical Electronics of Masaryk University, Brno, Czech Republic, EU,
romanpribyl@mail.muni.cz

https://doi.org/10.37904/nanocon.2019.8749

Abstract

In the present work we focused on the development of a low pressure capacitively coupled radio-frequency PECVD reactor for preparation of plasma-polymer thin films from organosilazane precursors. The dependence of the film growth from hexamethyldisilazane (HMDSZ, $SiN_2C_6H_{19}$) and oxygen containing mixtures on the deposition parameters was studied. The time evolution of the negative self bias voltage on the thin film growth was studied. It was found, that the changes in the self bias voltage significantly influenced the surface structure and the properties of the growing films. The mechanical properties of the films were studied using nanoindentation technique and the surface structure was studied using atomic force microscopy (AFM).

Keywords: PECVD, nanoindentation, profilometry, confocal microscopy, AFM

1. INTRODUCTION

The plasma enhanced chemical vapor deposition (PECVD) from silicon containing organic precursors is a highly versatile technique, which enables to prepare thin films in a very wide range of functional properties simply by means of the variation of deposition parameters. The resulting properties of the thin films are determined by their chemical structure and atomic composition. As has been shown in many publications [1-9], it is possible to prepare thin layers with extreme physical properties, such as high hardness, which may be higher, than that of the bulk material, high elasticity and fracture resistance, increased (or reduced) surface free energy, advantageous electrical, optical or thermal properties. For the application of these layers in the industry, it is important that the thin film preparation process is reproducible. This requires understanding the nature of the dominant parameters and processes that determine the resulting chemical structure and layer composition in order to optimize the deposition process. The parameters of prepared films may be varied by means of the main deposition parameters such the applied power, the bias voltage on the substrate holder, the deposition pressure, the deposition temperature, flow rates and flow rate ratios of precursors and base gases and the temperature of the monomers [10-13]. However, instead of the above listed parameters the geometry of the plasma reactor (reactor volume, size and distance of electrodes, the geometry and the method of introducing precursor gases into the apparatus, etc.) may play crucial role on the properties, film growth rates and the quality of the prepared films. In the present work we focused on the development and optimization of a low pressure capacitively coupled radiofrequency PECVD reactor for preparation of oxygen containing plasma-polymer thin films. We focused on the study of the dependence of the film growth from HMDSZ containing mixtures on the deposition parameters.

2. EXPERIMENTAL DETAILS

2.1. Thin film deposition

The PECVD chamber is made from stainless steel (see **Figure 1**). The volume of used chamber was determined on the basis of the pressure increase in the evacuated chamber with pumping valve closed during introduction of defined flow of nitrogen (S was in range from 10 to 30 sccm, 99.99% purity). This measurement

was made in the pressure range from 5 to 50 Pa with different times of pressure increase. The pressure was measured by capacity gauge Leybold CR090 (1 Torr), and the volume of the chamber was 23500 cm^3. The deposition system consists of two parallel stainless steel electrodes with the same diameter of 10.0 cm which are distant from each other at 5.5 cm. The lower electrode was connected to power supply Dressler CESAR 300W and the upper electrode was grounded. Because the chamber walls were grounded too, the created glow discharge was asymmetric. All gases are supplied through ring with small holes and inner diameter 0.6 cm, which is located over upper electrode (see **Figure 1**). All gas paths were designed with respect to the flow rate used, that means that gases with higher flow rate entrains gases with lower flow rate, this aspect is very important for accurate measurement of total flow rate and reproducibility of deposited thin films (other designs could lead to precursor condensation etc.).

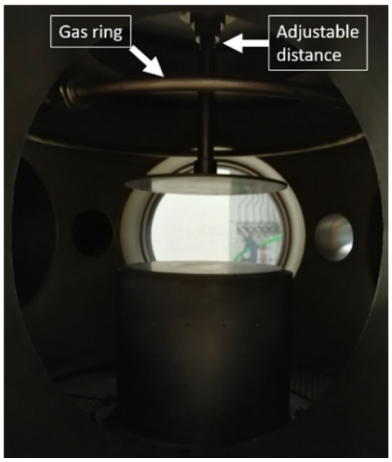

Figure 1 Insight inside deposition chamber with detail on gas ring

Application of organosilazane precursor (HMDSZ) in combination with the support gas (oxygen) enabled us to create ideal conditions for formation of dusty plasma. The dusty plasma is characterized by creating a larger particles or clusters of particles in plasma volume. Due to incorporation of growing particles, it is possible to make thin films with unique properties and high film growth rate. The dust particles and clusters are deposited at all chamber surface and this phenomenon can affect the self-bias voltage during the deposition. Therefore, the same procedure was used to treat chamber walls and electrodes prior to the main deposition process to maintain the same starting conditions for all depositions. The films characterized in the present work were made with the same supplied power (25 W), flow rate of HMDSZ (2 sccm) and O_2 (5 sccm), only with the deposition times were varied (see **Table 1**). Before each deposition the substrates were cleaned in argon plasma with supplied power of 50 W for 5 minutes.

2.2. Mechanical properties

The mechanical properties were examined using indentation techniques. Measurements of the 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 done using a Hysitron TI 950 nanoindentor equipped with diamond Berkovich tip [14]. The quasistatic loading regime with 33 unloading segments was used to evaluate the depth dependence of the mechanical properties. The maximum load for the loading segments was in the range from 0.1 to 11 mN.

2.3. Surface characterization techniques

For determination thickness of deposited films we used stylus profilometer Bruker type DektakXT - a small part of deposited film was removed to reveal the interface between the deposited film and the silicon substrate. Surface characterization was made by AFM (Ntegra Prima NT-MDT) and confocal microscopy (LEXT OLS4000 3D).

3. RESULTS AND DISSCUSSION

3.1. Surface's morphology

Confocal microscopy was used to determine visible differences in surface morphology between the thin films deposited with various deposition times. From the optical images (see **Figure 2**) of the as-deposited films it is visible, that films with higher deposition time have more rough surface due to increased amount of dust

deposited on substrate. Most of the dust clusters deposited on the film surface is weakly bounded to the film surface and can be removed by compressed air.

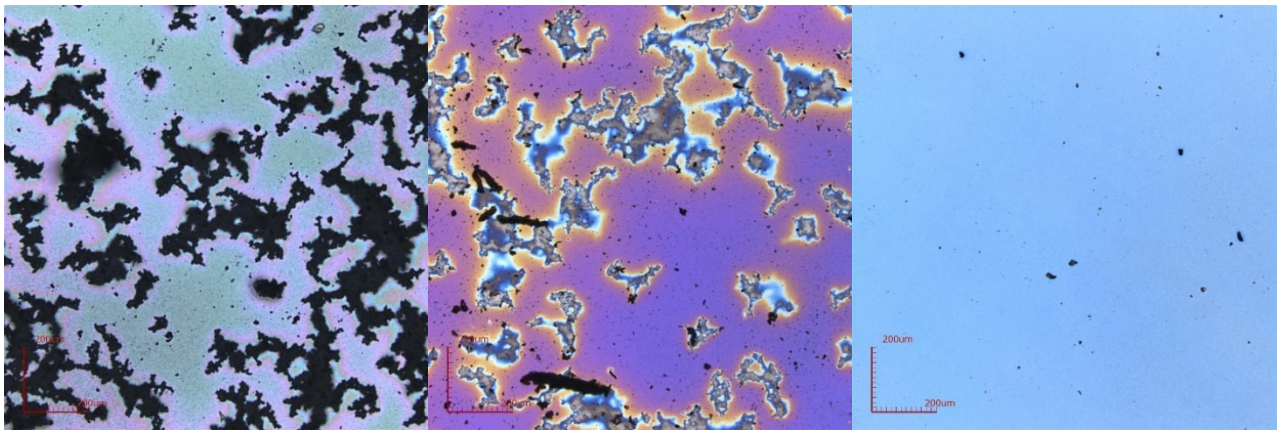

Figure 2 Optical images of deposited thin films taken with confocal microscopy with 10x zoom. From the left side: deposition time 10 min, 2 min and 0.5 min (area 1280x1280 μm).

After removal of the deposited dust we measured the thickness of thin films with stylus profilometer. This method was used due to the fact, that polymer thin films prepared in dusty plasma exhibit non-homogenities through film thickness what can lead to nontrivial dependency of refractive index and difficult evaluation of of film thickness using optical measurements. **Table 1** summarizes the measured thickness and the calculated deposition rate of the deposited films.

Table 1 Summary of the deposited thin films and their thicknesses

Deposition time [min]	10	5	2	1	0.5
Film thickness [nm]	1262 ± 40	712 ± 30	310 ± 30	260 ± 20	150 ± 10
Deposition rate [nm/min]	126	142	155	260	304

From **Table 1** it is clearly visible, that the deposition rate decreased with increased time of the deposition. For more detailed study of the surface structure atomic force microscopy (AFM) was used. Examples of the AFM images for films with three different deposition times are shown in **Figure 3**.

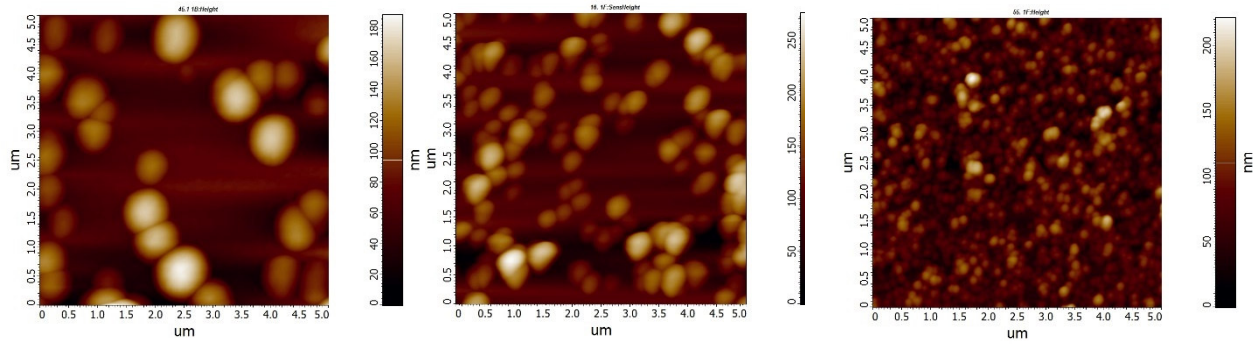

Figure 3 AFM images of the deposited thin films. From the left side: deposition time 10, 2 and 0.5 minutes.

From the AFM images it is clear, that the surface properties were significantly influenced with the deposition time. The particle size increased, on the other hand the particle density on the sample surface decreased.

These changes were closely related to the self-bias voltage value evolution during the deposition. The self bias voltage data were automatically recorded during the whole deposition. In case of all depositions the self-bias voltage had rising tendency (from -90 to -20 V for 10 minutes deposition) with increasing deposition time. According to our studies, the self bias voltage at the beginning of the deposition may be influenced by the state of the reactor walls and the electrodes. Therefore we have also to count with the influence of the pre-deposition process because the creation and the development of dusty plasma is highly susceptible to the type of the pre-deposited film on vacuum chamber walls and electrodes. In order to keep the self-bias values reproducible, in the first step we deposited a film on the chamber walls and the electrodes under the same plasma conditions as in the second step dealing with deposition of films on silicon substrates.

3.2. Mechanical properties of deposited thin films

In **Figure 4** the hardness and elastic modulus obtained on the most thick film (1262 ± 40 nm) can be seen. The hardness and elastic modulus values obtained for indentation depths up to 100 nm are approx. 1.25 GPa and 7 GPa, respectively. These values are typical for plasma-polymer thin films. However, in case of soft thin films on hard substrates, the influence of the substrate hardness on the measured data starts approximately from the half of the film thickness. According to the **Figure 4** the hardness increase starts much earlier, that means, that the film exhibited gradually decreasing hardness with increasing deposition time, probably because of the increasing size of dust particles embedding into the amorphous matrix. Because of their nanocomposite character the films showed significant elastic as well as anelastic (time dependent reversible deformation) behaviour, the indentation imprints tended to heal out during the unloading or after some time after the of the indentation test.

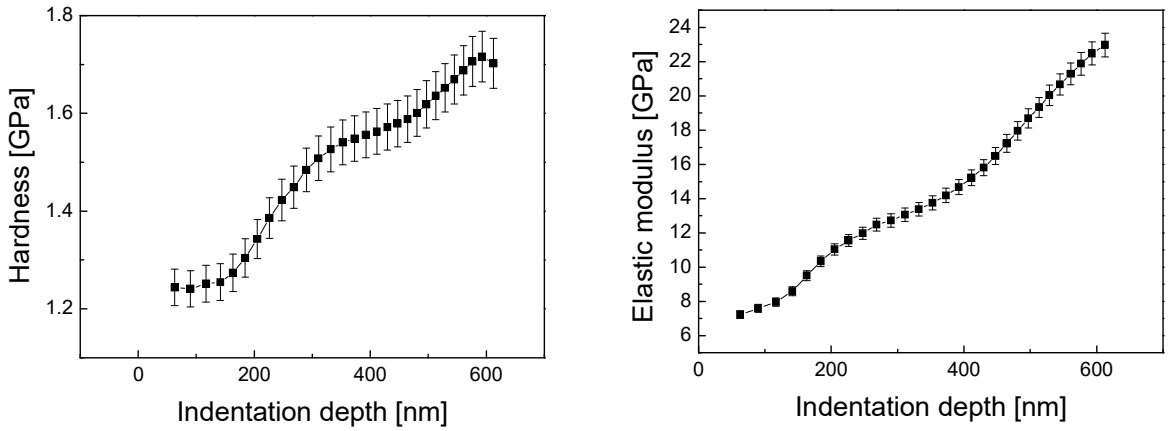

Figure 4 Dependence of the hardness (on the left) and the elastic modulus on the indentation depth measured on the film which was deposited 10 minutes (the film thickness was 1262 ± 40 nm)

4. CONCLUSION

New PECVD system was developed for preparation of plasma polymer nanocomposite films from mixtures of hexamethyldisilazane and oxygen. The films were prepared under dusty plasma conditions. It was found, that the surface structure of the films depends strongly on the deposition time because of the time evolution of the DC self-bias voltage. With the decrease of the absolute value of self-bias voltage increased the dust particle size in the plasma volume what led to decrease of the hardness and the elastic modulus of the prepared films. The film showed high elastic as well as anelastic recovery.

ACKNOWLEDGEMENTS

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.

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