

Deposition of Hydrophobic Polymer Films by Atmospheric Pressure Plasma Polymerization

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Abstract. The hydrophobic polymer films have been deposited onto glass substrates at atmospheric pressure by means of Plasma-polymerization process. The hexamethyl-disiloxane (HMDSO) organosilicon monomer was used as precursor for plasma polymerization in nitrogen working gas. As a source of non-equilibrium non-thermal plasma the novel type of coplanar DBD was used. The hydrophobic treatment of glass slides was stable-in-time and has passed through boiling test. The results indicate the possibility to deposit smooth pp-HMDSO thin films at atmospheric pressure.

Introduction

Generation of low-temperature, non-isothermal plasma is under great investigation because of a lot of applications in the field of material surface treatment, surface activation and functionalization of many different material's surfaces. The non-isothermal, low-temperature plasmas, as multi-component systems, provide multiple temperatures related to different particles. In many non-thermal plasma systems, electron temperature often significantly exceeds the heavy particle temperature ($T_e \gg T_0$). In the other words, electron temperature is about 1 eV (about 10,000 K), while the heavy particle temperature (gas temperature) is as low as room temperature. It implies that ionization and chemical processes in non-thermal plasma are directly determined by electron temperature. Moreover, the temperature difference between electrons and heavy neutral particles is valuable for plasma surface treatment without substrate surface damage.

In this study the thin polymer films on glass substrates from HMDSO monomer were deposited. The hydrophobic films were prepared at atmospheric pressure by plasma polymerization activated by non-isothermal plasma generated by a special type of coplanar DBD. Coated layers of similar properties are suitable for barrier or protective films and could be used for biocompatible applications [Fridman, 2008]. We have focused on studying plasma polymerization from different parameters and discharge characteristics point of view. Plasma-polymers, the result products of plasma polymerization, are highly branched and highly cross-linked. The resulting properties of new plasma polymers are unique and very often completely different from their "classic" counterparts. The surface-adhesion-improvement layers, better scratch resistance coatings are typical application of these new plasma polymer layers. For plasma polymerization it is typical to operate with many adjustable parameters, compared with the conventional polymerization. This results in appropriate process optimization to deposit new plasma polymer materials.

Experimental Setup

For plasma polymerization studies a special reactor was constructed (Figure 1). As the plasma source the Diffuse Coplanar Surface Barrier Discharge (DCSBD) [Černák *et al.*, 2009 and 2011] was used. This novel type of dielectric barrier discharge was fed by high voltage source (LIFETECH, s.r.o., Brno, Czech Republic) providing AC signal with voltage amplitudes up to 10 kV and frequency 12–16 kHz. The DCSBD plasma source generates the thin surface layer of plasma at atmospheric pressure at ambient air.

The voltage and current waveforms were measured according to the scheme in Figure 2 using the high-voltage probes Tektronix P6015A (1000X 3 pF 100 M Ω , attenuation for voltage inputs 1:1000) and the Rogowski coil (PEARSON ELECTRONIC 4100). Electric signals were processed by digital oscilloscope Tektronix TDS 2024 (bandwidth 200 MHz). For power input control from electrical system during all experiments the digital wattmeter FKtechnics was used.

In plexiglass reactor chamber a movable cart which held and moved a sample above DCSBD plasma was placed. The distance of sample's surface from ceramic surface of coplanar discharge could be adjusted as well as the velocity of the cart (Figure 1). The DCSBD discharge generates plasma in the form of "H" shaped filaments, but the plasma is visually macroscopically uniform and diffuse. To ensure more homogeneous treatment of samples the cart was moving over plasma by constant velocity. This "dynamic mode" enables to set up deposition time for plasma polymerization.

The samples were polymerized in N_2 /HMDSO mixture vapour. The *hexamethyldisiloxane* monomer (HMDSO; $C_6H_{18}OSi_2$, $(CH_3)_3Si-O-Si(CH_3)_3$; as-received from Merck company, Germany) for plasma polymerization was used. The monomer was let into reactor chamber by the nitrogen carrier gas (5.0). A N_2 /HMDSO mixture was prepared by system with two thermal mass flow meter controllers RED-Y (the pure nitrogen line was adjusted by flow meter with max. flow of $10\text{ l}\cdot\text{min}^{-1}$; the second N_2 /HMDSO mixture line was controlled by flow meter with the range up to $2\text{ l}\cdot\text{min}^{-1}$) (Figure 3). The monomer temperature was controlled by thermocouple sensor.

As the samples for plasma polymerization coatings the glass slides for optical microscopy with dimensions $25.85 \times 75.9 \times 1.0\text{ mm}$ were used. The surface of as-received samples was covered with organic and anorganic contamination. To ensure the same surface properties of substrates, every glass sample was cleaned before every experiment by this chemical cleaning procedure:

- 5-minutes cleaning in acetone in ultrasonic bath,
- 5-minutes cleaning in isopropyl-alcohol in ultrasonic bath,
- 5-minutes cleaning in distilled water in ultrasonic bath.

After each cleaning step each sample has been dried with nitrogen gas stream.

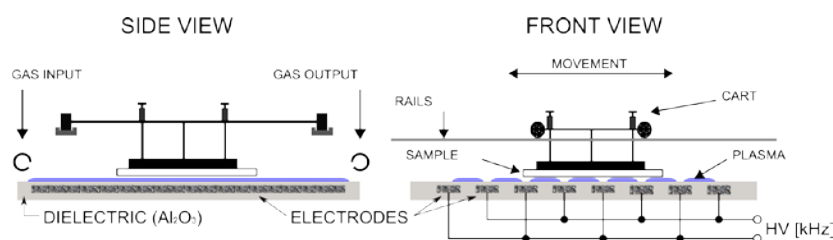


Figure 1. Plasma reactor based on DCSBD for plasma polymerization.

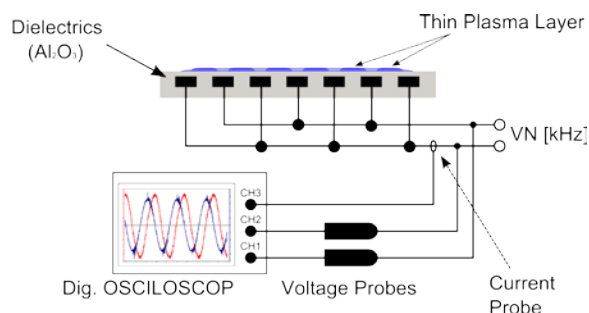


Figure 2. The scheme of electrical measurements.

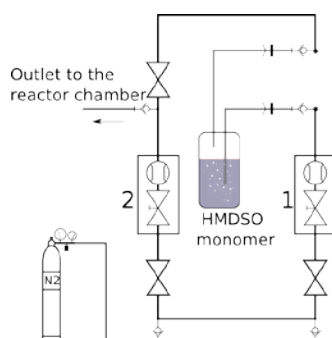


Figure 3. The scheme of gas system for N_2 /HMDSO mixture preparation. 1—flow meter for monomer mixture-pipe and flow meter 2 for pure nitrogen-pipe.

Results

Electrical and optical characteristics of DCSBD

The plasma of Diffuse Coplanar Surface Barrier Discharge is created by microfilaments, however the discharge burns in macroscopic diffuse character. The discharge burns also in oxygen, but in nitrogen the DCSBD plasma is more uniform and diffuse [Černák *et al.*, 2009].

Since we have been working with carrier gas supplied with HMDSO monomer to create N_2 /HMDSO mixture we could expect a transition to more filamentary character of DCSBD plasma. Actually, no visually change in filamentary – diffuse range of plasma in pure nitrogen, in ambient air, nor in N_2 /HMDSO mixture was observed. The DCSBD plasma had macroscopically homogeneous, diffuse character all the time. In Figure 4b there are I–U characteristics of plasma burned in N_2 /HMDSO mixture (monomer concentration in N_2 $c = 0.147 \text{ mmol}\cdot\text{l}^{-1}$). As it can be seen, the current peaks of microdischarges for N_2 /HMDSO plasma are a bit significant. The visual character of DCSBD plasma over the time of experiment was still quite uniform so the overall character of DCSBD discharge is not influenced by HMDSO monomer admixture to nitrogen carrier gas as it is shown in Figure 4a. It is important to emphasize that this observation applies only to the experiments for nitrogen carrier gas with HMDSO admixture. We expect other observation for other monomers because of different fragmentation mechanism and reaction chemistry at all.

According to previous measurements [Černák *et al.*, 2009] DCSBD plasma radiates the most intensive in the near UV spectral range. For spectroscopic measurements the *Avantes spectrometer* – 2048 TEC (Thermo-Electric Cooled) with spectral range from 300 nm to 400 nm and with spectral resolution of 20 px/nm was used. The plasma emission spectrum generated by DCSBD was measured in nitrogen (with the flow of $5 \text{ l}\cdot\text{min}^{-1}$). The measured optical spectrum we recorded according the power input in the range from 200 W to 300 W. The optical signal was shooting (scanned) in two positions—the space directly above the electrode or from the space between two neighbouring electrodes. The spectral lines in the gained spectrum were analyzed by Spectrum Analyzer 1.7 [Navrátil *et al.*, 2006] software. The goal of our optical measurement was to calculate rotational (T_{rot}) and vibrational temperatures (T_{vib}) for nitrogen plasma (Figure 5b). These calculations were based on spectrum simulations of Nitrogen Second Positive System $C^3\Pi_u \rightarrow B^3\Pi_g$; in software *Specair 2.2* [Laux, 2002].

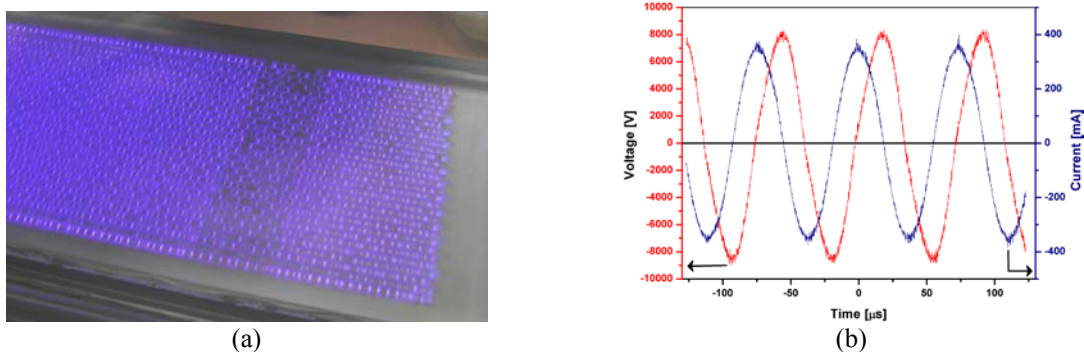


Figure 4. (a) The picture of DCSBD plasma in N_2 /HMDSO mixture (monomer concentration in N_2 $c = 0.147 \text{ mmol}\cdot\text{l}^{-1}$; total mixture flow of $6 \text{ l}\cdot\text{min}^{-1}$); (b) The I(t)/U(t) characteristics of DCSBD plasma with input power of 270 W in N_2 /HMDSO for the same conditions as in the case a). In the center of left picture thin dielectric barrier for better “H” shaped microdischarge illustration was placed.

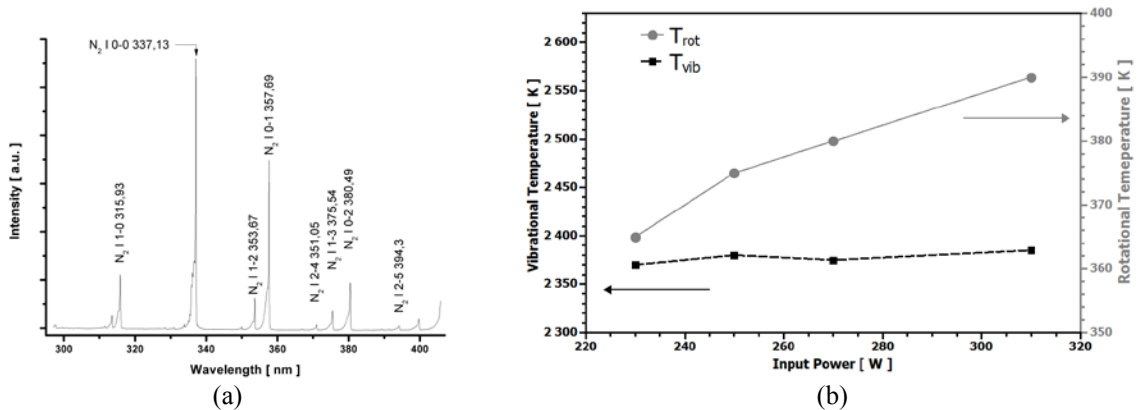


Figure 5. (a) The spectrum of DCSBD plasma; (b) The dependence of T_{rot} and T_{vib} on the input power.

Table 1. Temperatures in DCSBD plasma calculated from optical signal measured in the space above electrode.

Input Power [W]	T _{rot} [K]	T _{vib} [K]
230	365	2370
250	375	2380
270	380	2375
310	390	2385

We proved that in the power input range from 200 W to 300 W the DCSBD plasma is highly non-isothermal (see Table 1). More precisely, the vibrational temperature in the space directly above electrode was estimated on $2375 \text{ K} \pm 50 \text{ K}$ (for power input 270 W). It corresponds to energy of $\approx 0.2 \text{ eV}$ and according to distribution function the temperature for electron is surely higher. The rotational temperature corresponding to the temperature of gas was estimated on $380 \text{ K} \pm 50 \text{ K}$ (T_{rot} is approximately 110°C , which corresponds to energy of $\approx 0.03 \text{ eV}$).

pp-HMDSO Layers Characterization

As the result of plasma polymerization, the highly branched and highly cross-linked materials due to radical fragmentation mechanism of polymerization are deposited. The plasma polymerized films are in this paper marked as pp-HMDSO films to emphasize their *plasma-polymer* character.

The primary goal of this work was the optimization of the process parameters for stable hydrophobic layers deposition on the glass substrates. As the representative value for hydrophobic properties quantification the Water Contact Angle (WCA) was chosen. The contact angle measurements were done by See System device [Buršíková et al., 2004]. As the testing liquid distilled water was used and data by single-liquid method was evaluated.

Plasma polymerization depends on various variables so it is quite complex process. This work is focused mainly on studying the following parameters which affect plasma polymerization process:

- Monomer concentration in nitrogen carrier gas
- Plasma-polymerization treatment time
- Input power
- Distance of the sample from the discharge surface.

These parameters are important also from another point of view. An appropriate choice of optimal plasma regime, monomer concentration and treatment time are crucial for serious application of every plasma-chemical process because of efficiency and low cost processing.

The time of polymerization was varied from 15 seconds to 90 seconds. The *hexamethyldisiloxane* monomer concentration in N_2/HMDSO mixture in the range from $c_{\text{min}} = 0.017 \text{ mmol}\cdot\text{l}^{-1}$ to $c_{\text{max}} = 0.252 \text{ mmol}\cdot\text{l}^{-1}$ through pure nitrogen flow and N_2/HMDSO mixture flow was changed. The input power was set from 200 W to 300 W.

The typical characteristic of DCSBD is to increase the diffuse plasma at the expense of the filamentary one with the increasing input power, while optically the DCSBD plasma remains still macroscopically homogeneous. During plasma polymerization process the input power is consumed for plasma generation and for monomer fragmentation. The minimal input power was set up according to complete plasma generation on the whole alumina ceramic surface of DCSBD with macroscopic homogeneous plasma.

The distance of glass samples over the alumina ceramics surface was set to the values of 0.2 mm; 0.3 mm; 0.5 mm and 1 mm to achieve the best hydrophobic treatment. For completeness, the thickness of DCSBD plasma is on the order of $\approx 0.1 \text{ mm}$ [Černák et al., 2009]. We can conclude that the optimal distance might be the value of 0.3 mm. At the distances 0.2 mm and less, the coated surface is in direct contact with plasma filaments and it led to non-homogeneous polymer-layer deposition with quite a lot of visible defects.

The contact angle measurements of the pp-HMDSO films were performed approximately 20 minutes after the deposition. Deposition times exceeding 60 sec. resulted in the non-homogeneous films. On the other hand, the polymerization time less than 30 seconds did not produce films with satisfactory hydrophobic properties.

According to the values of variables, the values of contact angles measured on polymer layers varied within the range of 60° to 105° . Repeating several series of experiments, we tried to optimize the process parameters in order to deposit layers with the best hydrophobic properties.

The ageing effect and the boiling test

The stability of deposited hydrophobic films was evaluated by boiling test and moreover we monitored the possible Ageing effect. The hydrophobic properties analyzed by contact angle measurement immediately after the polymerization showed high dispersion of WCA values. The changes of contact angles were monitored 120 hours after the layer deposition. In Figure 6a there is very clearly visible reduction of dispersion for contact

angle values, while the average WCA value remains more or less constant. In conclusion, we didn't observed so-call Ageing effect. Actually, even after 120 hours (5 days) the contact angles were above 90 degrees while staying at ambient conditions.

The boiling test proved the hydrophobic stability of pp-HMDSO layers even after 120-minutes boiling in distilled water (temperature $\approx 95\text{--}100\text{ }^\circ\text{C}$) as can be seen in Figure 6b. In Figures 6a,b are plotted contact angles measured on samples deposited at optimal values of process parameters described at the end of this section.

Based on the results of hydrophobic treatment presented earlier we specified the so-called “*Optimal values of process parameters*” as follows:

- Treatment time: 60 seconds (the time of plasma polymerization)
- Input power: 270 W
- Distance of glass samples from alumina ceramic surface: 0.3 mm
- Relative flow of N_2/HMDSO mixture through reactor chamber $q_{\text{rel}} = 16.7\%$, i.e. monomer concentration of $c = 0.147\text{ mmol}\cdot\text{l}^{-1}$. Relative flow q_{rel} is calculated as the fraction of N_2/HMDSO mixture flow through flow meter #1 (see Figure 3 in the section *Experimental Setup*) to the total flow of nitrogen.

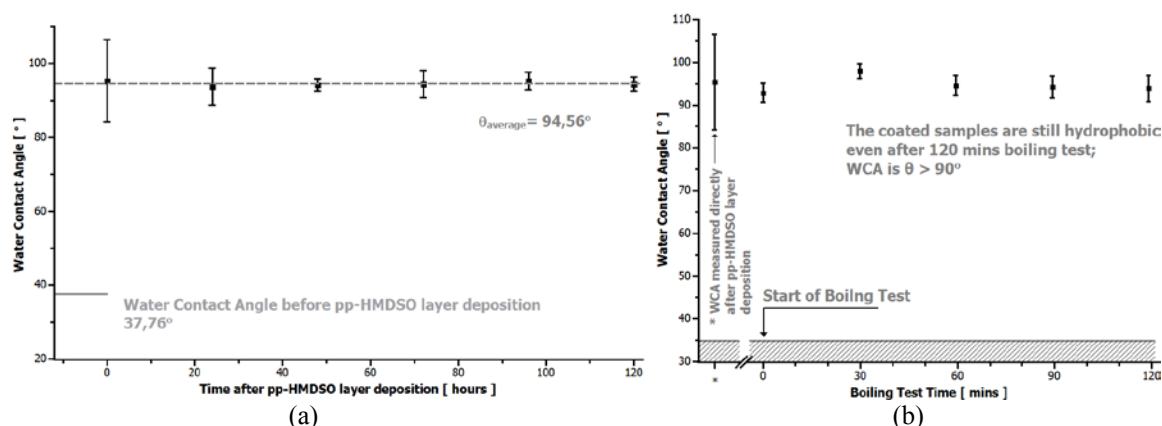


Figure 6. The stability of deposited pp-HMDSO films analyzed by (a) ageing of polymer layers with time; (b) boiling test. The films were deposited at optimal values of process parameters (read next paragraph).

Discussion

The polymer pp-HMDSO layers deposition on glass substrates with process and parameters optimization was performed. The optimal values for monomer concentration in N_2/HMDSO mixture, polymerization time and discharge input power have been sought. The contact angle analysis was chosen as the primary evaluation parameter (while it is fast, reliable, available).

One undesirable effect during DCSBD plasma enhanced polymerization was observed. The polymer layer on the Al_2O_3 dielectric where DCSBD plasma burns was deposited. This useless deposition was observed only in places where plasma burned and not elsewhere, not on the inner reactor surfaces or gas inlet/outlet tubes. It is obvious, that this useless deposition have been processed only in the places where plasma was generated and monomer fragmented by high-energetic electrons. The properties of this undesired layer was determined by the operational parameters, e.g. for higher monomer concentrations this layer was thicker. On the other hand, in case of lower monomer concentrations in N_2/HMDSO mixture than $c = 0.017\text{ mmol}\cdot\text{l}^{-1}$ no coherent deposits on the alumina ceramic's surface was deposited.

The Al_2O_3 dielectric barrier is heated up during the operation time. The temperature impact on the plasma polymerization process will be under the next investigation as well as the undesirable but interesting effect of layer deposition on discharge surface.

In [Paulussen *et al.*, 2003] the polymer layers on polished SiO_2 surface of silicon were deposited in nitrogen plasma generated by dielectric barrier discharge with two planar electrodes. After the 2 minutes polymerization from N_2/HMDSO mixture (carrier gas flow $151\cdot\text{min}^{-1}$; precursor mixture flow $11\cdot\text{min}^{-1}$) the hydrophobic layers with contact angle of 105.6° were deposited. Layers with similar values of contact angles ($100\text{--}110^\circ$) we were able to deposit at half polymerization time instead. Unfortunately, the authors don't specify the input power to discharge what would be surely interesting to compare.

According to the optical emission spectroscopy measurements we proved that DCSBD plasma is far from thermodynamic equilibrium. DCSBD plasma source provides high-energetic electrons, while keeping bulk temperature close to room temperature. The highest energy in non-thermal DCSBD plasma (i.e. electron energy)

is on the order of magnitude of 1 eV. It is only about 10% of required monomer fragmentation energy which is about 10 eV.

This observation is consistent with the general rule found by Zeldovich and Frank-Kamenetsky for atoms and small molecules in chemical kinetics: The temperature required for a chemical process is typically about 10% of the total required energy, which is the Arrhenius activation energy [Fridman, 2008].

Conclusion

The possibility to employ the plasma generated by DCSBD discharge for atmospheric pressure plasma polymerization of HMDSO monomer in nitrogen carrier gas was studied. The process of plasma polymerization is quite a complex, with a plenty of free parameters. The aim of this work was to optimize some selected parameters such as monomer concentration in carrier gas, input power to the discharge and the time of polymerization for the best hydrophobic layers on the substrates. It shows that a crucial important parameter for layer quality and its homogeneity is to set up the proper distance of sample from discharge surface. The optimal process parameters for selected variables and its values were outlined.

The stable hydrophobic pp-HMDSO thin layers were coated on the glass substrates. The ageing effect was not observed. The stability of hydrophobic coatings was monitored up to 120 hours after plasma polymerization deposition. The average value of contact angle remained constant with significant decrease of dispersion values. Moreover, the coated samples pass through the 120 minutes boiling test in distilled water.

The plasma polymerization of HMDSO was activated by plasma generated by DCSBD. The non-isothermal, low-temperature plasma was ignited in N₂/HMDSO mixture, unless no transition to more filamentary regime was observed. The used plasma source generated macroscopically diffuse plasma at the input power over 200 W.

The numeric simulation of UV spectrum (300–400 nm) for rotational and vibrational spectrum was carried out. We concluded that at input power in the range 200–300 W (and higher) the characteristic temperatures remains constant (± 50 K). Moreover we significantly showed that DCSBD plasma is non-isothermal with vibrational temperature of 2375 ± 50 K, while the temperature of gas remains 380 ± 50 K.

The obtained results have valuable importance for DCSBD optimization not only for DCSBD plasma enhanced polymerization. The results suggest new options how to improve the deposition process and show which phenomena should be studied in details in the future.

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