

Fabrication of Hydrophobic Films from OFCB Monomer by Plasma Polymerization at Atmospheric Pressure

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Abstract. Octafluorocyclobutane gaseous monomer is used to fabricate hydrophobic films on glass substrates. The plasma polymerization deposition process was carried out at atmospheric pressure in nitrogen carrier gas. The coplanar type of DBD plasma source was used to activate PE-CVD process. The preliminary results are published where stable (4 days) hydrophobic layers have been coated with contact angle of values about 100 degrees. The prepared films were analysed by contact angle measurements, Fourier transform infrared spectroscopy and moreover simple test of stability was done to evaluate prepared samples. These surface analyses confirmed the applicability of the coplanar type of DBD plasma source for deposition of octafluorocyclobutane hydrophobic films at atmospheric pressure.

Introduction

The unceasing interest for plasma technologies still continues for many decades. The generation of low-temperature, non-isothermal plasma is under great investigation because of a lot of applications has developed in the field of material plasma surface treatment. The applications concern the plasma surface modifications, ozone generation or gas reformation as well as light sources [Pietsch and Gibalov, 1998; Goosens *et al.*, 2001; Wagner *et al.*, 2003]. Atmospheric pressure plasma processes, compared to low pressure techniques or conventional chemical processes, offer advantages which are not negligible for industrial applications. Typical benefits are e.g. short reaction times, production of unique plasma modifications or more environmentally friendly techniques [Kogelschatz, 2003]. The interest on the non-isothermal, low-temperature plasmas is given by providing multiple temperatures related to different particles. In many non-thermal plasma systems, electron temperature often significantly exceeds the heavy particle temperature ($T_e \gg T_0$). While heavy particle temperature (gas temperature) can be as low as room temperature, the electron temperature is of the order of several eV (about 10 000 K). It implies that ionization and chemical processes in non-thermal plasma are directly determined by electron collisions and by the electron energy distribution functions. Moreover, the low energy heavy neutral particles cannot damage substrate surface.

In this study thin films on glass substrates from *octafluorocyclobutane* (OFCB, C_4F_8) monomer were deposited. The hydrophobic plasma polymerized films (pp-OFCB films) were prepared at atmospheric pressure by plasma polymerization activated by non-isothermal plasma generated by a special type of coplanar dielectric barrier discharge.

Plasma polymerization and OFCB monomer plasma polymerization

Plasma-enhanced chemical vapour deposition (PE-CVD) employs the conversion of gaseous monomer into reactive radicals, ions and neutral molecules and subsequent deposition of these precursors onto the substrate surface. PE-CVD films offers the promise of dense cross-linked films [Grant *et al.*, 2004]. Films formed in this way afterwards exhibit strong adhesion, low pinhole density and high surface uniformity [Wasilik and Chan, 2004]. Plasma polymerization using PE-CVD is a dry deposition technique, suitable for automation, can be run at room temperature, and in general can be used for deposition on both planar and curved surfaces [Grant *et al.*, 2004]. Compared to conventional wet techniques, plasma polymerization generates less waste and allows polymers to be formed from non-conventional precursors. Plasma polymerization is known as easy method how to modify material surfaces through the deposition of a thin polymer film which promotes good adhesion between films to substrate [Chan, 1994]. The plasma polymerization deposition process can be easily controlled by treatment conditions [Friedman, 2008]. Adjusting the PE-CVD processing parameters e.g. input energy, reaction time, proper choice of plasma reactor type, also allows for fine-tuning the chemistry and the thickness of films [Grant *et al.*, 2004]. For plasma polymerization it is typical to operate with many adjustable parameters, compared with the conventional polymerization, resulting in easy setting of treatment conditions and in appropriate process optimization.

Octafluorocyclobutane gas is well known in nanotechnology where is used as deposition gas and serves as etchant. Generally, the fluorocarbons have quite wide range of applications [Abadjieva *et al.*, 2012]. Fluorine containing plasmas are known to decrease surface energy and increase the hydrophobic behaviour of surfaces [Chan, 1994]. Fluorocarbon plasma seems to be an efficient tool to improve the frictional properties, since the produced Teflon-like surface film possess chemical inertness, low surface energy (non-wettable), excellent frictional properties, lower permeability, and relatively good thermal stability [Sedlacik *et al.*, 2012 and Biederman, 2004]. During a few last years there have been published some papers, where OFCB have been used for deposition of hydrophobic, Teflon-like coatings some of them even at atmospheric pressure [Abadjieva *et al.*, 2012 and Sedlacik *et al.*, 2012].

Motivation

In our previous papers we presented the deposition of pp-HMDSO polymer layer which were composed mainly on the methyl CH_x groups originated from *hexamethyldisiloxane* (HMDSO) precursor. We observed that during our plasma polymerization experiments the surface of dielectric barrier get coated as well by organic/inorganic based layer [Krumpolec *et al.*, 2013]. Similarly, this deposition effect was observed also for another precursor for plasma polymerization — *acrylic acid*. Therefore we intended to employ another precursor with different plasma polymerization mechanism. On the other hand, in our previous experiments with pp-HMDSO thin films deposition, we observed the influence of electrical input power, monomer concentration and total flow rate on the chemical composition of plasma polymers. Based on experiment conditions, there were created polymers with different fraction of C_yH_z organic species in SiO_x base.

According to Abadjieva's paper [2012] it is possible to achieve high flour content of the coating with OFCB as precursor. Moreover, in the cited paper the authors observed the plasma reactor walls coating with deposits during the experiments. The wall of the reactor has gone deposited with larger particles having exclusively C–F elemental composition.

As mentioned earlier, PE-CVD based deposition offers the promise of dense cross-linked films. This assumption we have observed during our previous experiments with pp-HMDSO layers deposition too. Unlike, the application of *octafluorocyclobutane* leads to reduction of the cross-linking effect in the plasma polymer film [Vinogradov and Lunk, 2005]. In general, for fluorocarbons in plasma higher CF_x/F ratio enhances polymerization while lower CF_x/F ratio promotes surface reactions and etching. Higher plasma power is known to create more fragmentation of the C_4F_8 monomers [d'Agostino, 1990]. For fluorine containing systems, surface reactions, etching and plasma polymerization can occur simultaneously [Yeo *et al.*, 2005].

Therefore, because of high F/C ratio, the OFCB monomer was chosen as the next precursor for studying the unwanted layer deposition on the DCSBD dielectric surface and plasma deposition applications. In this work we report the results of plasma polymerization deposition experiments with OFCB monomer onto glass samples.

Experimental setup

The plasma polymerization experiments have been carried out in special reactor (Figure 1). The *Diffuse Coplanar Surface Barrier Discharge* (DCSBD) [Černák *et al.*, 2009 and 2011] was used as the plasma source. This 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 20 kV (U_{p-p}) and frequency 15–18 kHz. The DCSBD plasma source generates the thin surface layer of plasma at atmospheric pressure at ambient air. This plasma source generates plasma in the form of “H” shaped filaments, but the plasma is still visually macroscopically uniform and diffuse. For power input control from electrical system the digital wattmeter FKtechnics was used during all experiments. The power input was measured as the total sum of electrical power into HV power source.

Our plexiglass reactor chamber contains a movable cart for planar samples. The distance of sample surface from ceramic surface of coplanar discharge could be adjusted as well as the velocity of the cart (Figure 1). During the experiments the cart is able to move above generated plasma with constant velocity. This “dynamic mode” enables to set up deposition time for plasma polymerization as well as to ensure more homogeneous sample treatment. A more detailed description of our plasma polymerization reactor have been outlined elsewhere [see Krumpolec *et al.*, 2012a].

The processing gas was a mixture of the carrier gas nitrogen (4.0) and the precursor OFCB. Compressed gaseous *octafluorocyclobutane* precursor (used directly without any further purification; from Linde Gas company, Germany) for plasma polymerization was used to fabricate hydrophobic pp-OFCB layers. The total flow rate of N_2 /OFCB mixture was controlled separately for nitrogen and gaseous OFCB monomer. The flow of nitrogen was controlled by thermal mass flow meter controller RED-Y, while for OFCB flow rate control the rotameter was chosen (Figure 1).

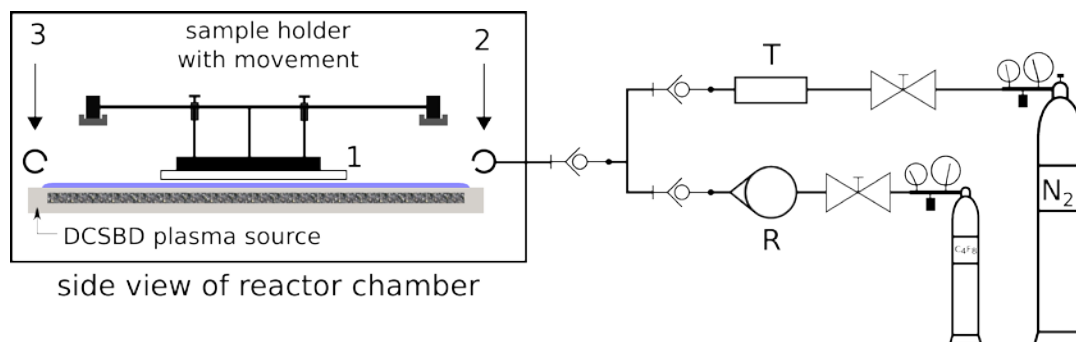


Figure 1. The sketch of plasma reactor based on DCSBD for plasma polymerization with gas control system for N_2 /OFCB mixture preparation. R — rotameter for pure OFCB monomer and thermal mass flow meter T for pure nitrogen-pipe; 1 — treated sample; 2 — gas inlet and 3 — gas outlet.

The hydrophobic C–F coating has been deposited onto glass substrates. Glass slides for optical microscopy with dimensions $25.85 \times 75.9 \times 1.0$ mm were used. The surface of as-received glass samples is inhomogeneous and covered with organic and inorganic contamination. To ensure the most equal surface properties of substrates as possible, every glass sample was cleaned before every experiment by next chemical cleaning procedure:

- 1st step: 5 — minutes cleaning in acetone in ultrasonic bath,
- 2nd step: 5 — minutes cleaning in isopropyl-alcohol in ultrasonic bath,
- 3rd step: 5 — minutes cleaning in de-ionised water (DI water) in ultrasonic bath.

After each cleaning step each sample has been dried with nitrogen (4.0) gas stream.

The hydrophobic pp-OFCB films on glass substrates were gained as result of plasma polymerization. The *Water Contact Angle* (WCA) was chosen as the representative value for hydrophobicity quantification. The contact angle measurements were done by See System device [Buršíková *et al.*, 2004]. The deionized (DI) water as testing liquid was used and data by single-liquid method were processed. Water droplets (2 μ l) were placed on the surface, and the formed CA was measured 30 seconds after deposition of droplet. All presented numeric results of contact angle measurements are statistic results of data collected from 20 measurements from 2 samples.

The FT-IR spectra were recorded by BRUKER VECTOR 22 spectrometer using diamond Attenuated Total Reflection with Diamond/ZnSe polarization accessory from MIRacle™ (PIKE Technologies). The diamond was set at 45 degrees and other measurement settings were 20 scans, resolution 4 cm^{-1} , measuring range $4000\text{--}500\text{ cm}^{-1}$. The data acquisition and processing software OPUS was applied to generate the thin film absorbance spectrum.

Results and discussion

In this work the plasma polymerized thin films from OFCB were deposited. Thin films were transparent in visible light and hydrophobic. We carried out series of experiments to specify the process parameters. Our previous experiments with plasma polymerization of HMDSO monomer [Krumpec *et al.*, 2012a and 2012b] were taken account, where nitrogen was used as plasma forming gas too. During plasma polymerization the input electrical power, deposition time, gas mixture concentration, location, and movement of sample in reactor and total flow rate were monitored. The experiments were performed at atmospheric pressure, and ambient temperature was between $20\text{--}22\text{ }^\circ\text{C}$.

In Table 1 are shown the results of contact angle measurements of pp-OFCB thin films, which were deposited by plasma polymerization controlled and set with parameters summarized in Table 2. The initial contact angle of DI water on the untreated glass samples reached the value around 49° . This WCA on reference sample seems too high whereas the properly cleaned glass has usually WCA around 30° . All WCA values are given with a tenth of degree accuracy because all values are average results of 20 individual measurements.

Table 1. Contact value data of pp-OFCB films on glass substrates.

Sample	Deposition time	Contact angle [$^\circ$]	+/- [$^\circ$]
OFCB- N_2 -300W-1min	60 s	100.3	5.9
OFCB- N_2 -300W-1min (measured 100 hours after experiment)	60 s	96.3	3.9
OFCB- N_2 -300W-2min	120 s	99.2	6.5
Reference substrate		48.7	2.7

Table 2. Summary of setup parameters of plasma-polymerization experiment.

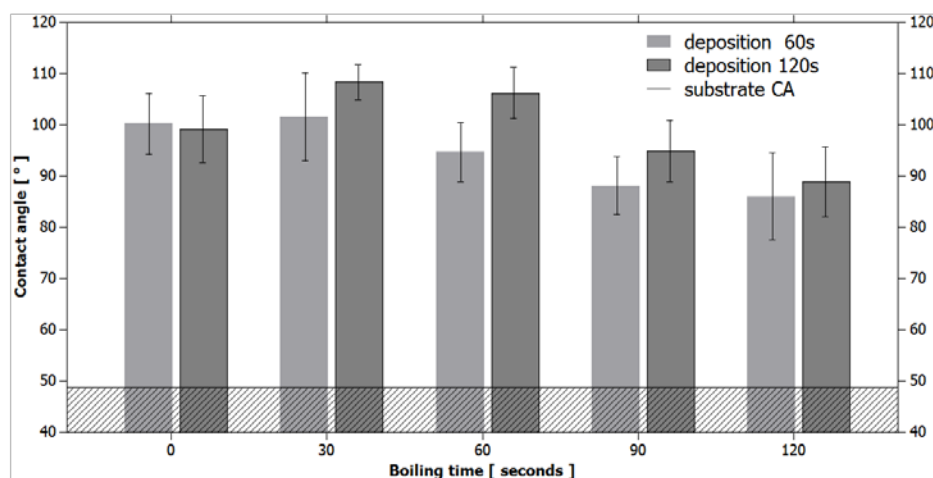
Treatment time (total time of plasma polymerization)	60 / 120 second s
Input power	300 W
Distance of glass samples from alumina ceramic surface	0.3 mm
N₂/OFCB gas mixture total flow (slm = standard liters per minute)	6 slm
OFCB flow (flow of pure OFCB monomer gas)	1 slm

In the first data row of Table 1 are given results of contact angle measurements of the pp-OFCB films. The values were measured approximately 30 minutes after the ends the deposition experiments. Immediately after the deposition the coated samples were stored under ambient conditions in glass boxes. The hydrophobic properties of pp-OFCB films were monitored during first 100 hours after the experiment. The CA values were quite stable in time and were not changed rapidly within this time period. We don't have data for longer time period because of we are not able to maintain the constant storage conditions for our samples in longer period. A double prolongation of deposition time has no effect on the hydrophobic properties of the prepared films as can be seen from Table 1 and compared 1st and 3rd data rows.

The stability of prepared thin films were also tested by the so-called boiling test. The polymerized samples were immersed in boiling water for 30 minutes and testing of contact angles was repeated. This experiment was performed four times again. This 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 2. Although the dispersion of WCA is in the range of $\pm (5\text{--}10)^{\circ}$, the mean WCA value remains more or less constant at the level above 90° .

For initial chemical evaluation of layers we used FT-IR spectroscopy to reveal the chemical composition of thin films. In Figure 3 we can see the absorbance of the signal against the wavenumber for two samples deposited during 1 minute and 2 minutes experiment and compared to untreated glass sample. We are able to determine the typical peaks for carbon — flour (C-F) or carbon — oxygen single or double bonds (C-O, C=O). During this plasma polymerization experiments no admixture of oxygen was used. The oxygen revealed in FT-IR spectra most likely comes from substrate. As we mentioned earlier, glass plates were used. We assume the surface OH species are activated on the glass surface during DCSBD plasma treatment [Lazović *et al.* 2008]. Our assumption is supported in higher wavenumber region where a marked growth of OH groups ($3600\text{--}3100\text{ cm}^{-1}$) can observed in FT-IR spectra of DCSBD plasma treated glass surface. In the case of pp-OFCB films the intensity of FT-IR signal in region ($3600\text{--}3100\text{ cm}^{-1}$) decrease, while we observe increasing of absorbance signal assigned to carbon-oxygen bonds (Figure 3).

This reactive species react with carbon and flour compounds creating bonds with oxygen revealed in FT-IR measurements. As the samples were stored at ambient air we assume that the oxygen in the polymer film origin from air too. From FT-IR absorbance spectrum it is clearly visible the difference in intensity of the fingerprint peaks. The samples are different in deposition time. Therefore the sample deposited 2 times longer with more intense spectrum is coated much more with plasma polymer.

**Figure 2.** The stability of deposited pp-OFCB films during boiling test. The boiling time „0“ seconds stands for CA measured before boiling test. The hatched area refers the CA of untreated glass sample surface.

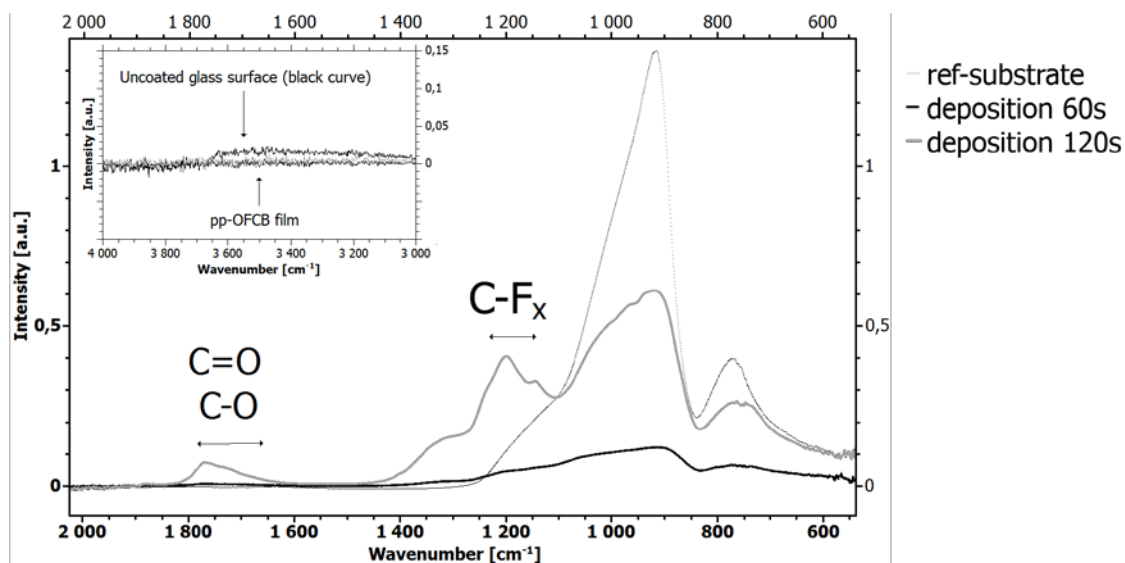


Figure 3. FT-IR absorbance spectra for two pp-OFCB films deposited at optimized plasma processing parameters for 1 minute (black) and 2 minutes (gray) respectively.

During the plasma polymerization in DCSBD plasma the coated sample is placed at some distance from generated plasma. Therefore, plasma polymerization reactions are conditioned by the presence of active radicals and most likely they occur through ion-radical reactions. As the process is carried out under atmospheric pressure, electrons play an important role. The DCSBD plasma ignited in N_2 /OFCB gas mixture seems to get more filamentary character to the plasma ignited in HMDSO or AAc monomer. The diffuse plasmas cover the whole surface over electrode with extensively visible small microfilaments. The worst homogeneity of N_2 /OFCB plasma doesn't impact on the homogeneous sample treatment while dynamic mode of plasma deposition process was chosen.

Conclusion

We proved sufficient PE-CVD thin film deposition by plasma polymerization in gas phase from N_2 /OFCB gas mixture activated DCSBD plasma source at atmospheric pressure. The stable hydrophobic pp-HMDSO thin layers were coated on the glass substrates. Presented first results show that we are able to deposit hydrophobic C-F layers where the contact angle of DI water was around (more than) 100° . The hydrophobness stability was controlled up to 100 hours (almost 5 days). The average value of contact angle remained quite constant. The ageing effect of pp-OFCB films was not pronounced. Moreover, the coated samples pass through the 120 minutes boiling test in distilled water where no significant decrease of WCA was observed.

The obtained results have contributed to the complex study of plasma generation in various monomer/gas mixtures ignited by DCSBD plasma. Presented results can be used for next DCSBD optimization not only for DCSBD plasma enhanced polymerization. Unlike to the plasma polymerization in N_2 /HMDSO gas mixture, the effect of unwanted layer deposition in N_2 /OFCB mixture was significantly smaller than described in paper [Krumpolec et al., 2013].

The more detailed study of DCSBD plasma ignited in N_2 /OFCB gas mixture is needed. Further work will be carried out to determine the actual thickness of the pp-OFCB layers and also to characterize the amount of fluorine in thin film. The deeper investigations of unwanted deposits on the dielectric surface are planned also for OFCB monomer.

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