# DEPOSITION AND CHARACTERIZATION OF THIN HYDROPHOBIC LAYERS USING ATMOSPHERIC-PRESSURE SURFACE BARRIER DISCHARGE

**PAVEL SŤAHEL*, VILMA BURŠÍKOVÁ, JAN ČECH, ZDENĚK NAVRÁTIL, and PETR KLOC**

*Masarykova Univerzita, Kotlářská 2, 611 37 Brno, Czech Republic*
*pstahel@physics.muni.cz*

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## 1. Introduction

The plasma technologies became very promising technique for surface engineering of solids. The wide spread low-pressure plasma applications[1–7] have to use expensive vacuum systems. That approach requires batch processing and inhibits the application of low-pressure plasma in larger industrial scale for treatment of low-cost materials, where in-line treatment of materials is necessary.

Several advantages of the surface modification of low-cost materials provide atmospheric-pressure plasma processing. The most significant advantages are: the expensive vacuum system is not necessary, processing times are reduced, and the scalability of plasma applications towards large-surface processing is simpler than in low-pressure plasma applications.

Recently, mainly atmospheric-pressure corona discharge or volume barrier discharge (VBD) devices are used for surface treatment of polymeric materials. In the case of VBD the requested plasma conditions are achieved only in small-volume plasma channels − streamers − developing perpendicularly to the surface of material. In that case the plasma is in a very limited contact with the surface resulting in low processing speeds, typically in the order of 1 m $min^{-1}$. Moreover, the localized arcing may result in the formation of pinholes in the material being treated. The using of atmospheric-pressure glow discharge (APGD) can surpass these disadvantages, however APGD is very sensitive to gas purity and optimization of electrode arrangement. These facts limit the applicability of APGD[8].

In this work the surface barrier discharge operated at atmospheric pressure was used for deposition of thin protective hydrophobic films on paper substrates.

This work has to demonstrate good protective properties of the films deposited by means of this technique. Variation of colorimetric parameters of paper substrates such as whiteness or yellowness caused by plasma deposition and the evolution of these parameters under intensive UV irradiation is shown too.

## 2. Experimental

The fluorinated (Teflon-like) materials are widely used for their low surface energy and low wettability. As precursor for thin film deposition the octafluorcyclobutane $C_4F_8$ was used. The $CF_4$ (ref.[7]) or fluortrimethylsilane[8] are reported in the literature as precursors too. The surface barrier discharge at atmospheric pressure was used for the deposition process. The discharge was ignited on the surface of the insulating mica plate, which was fully covered with metal electrode from one side, while the opposite side of the plate was covered with moving paper sample pressed to mica with rod electrode. The rod electrode consists of nine 100 mm long rotating rods, connected together with 9 mm spacing[9]. Between each two rods of the electrode two gas inlets were placed. The whole arrangement was placed into deposition chamber. The paper strips were carried through the discharge chamber with controlled speed. The surface power density was set within the range 0 to 1.0 W $cm^{-2}$. In this study the deposition time 90 s was kept constant as well as the concentration of $C_4F_8$ in nitrogen, i.e. 0.5 slpm of $C_4F_8$ in 10 slpm of pure nitrogen. As a substrate the filter paper was used. The discharge was studied by means of the optical emission spectroscopy. The discharge spectra were recorded using the Jobin-Yvon TRIAX 550 monochromator, equipped with the liquid nitrogen cooled CCD detector. The total surface free energy of samples $\gamma^{TOT}$ and its components $\gamma^{LW}$, $\gamma^{AB}$, $\gamma^{+}$, $\gamma^{-}$ were investigated by means of the sessile drop technique using the Surface Energy Evaluation System (http://www.advex-instruments.cz/). The contact angles were measured directly from the CCD camera images of the solid/liquid meniscus of a sessile drop set on a solid surface. The samples surface free energy and its components were calculated according to Lifshitz-Van der Waals/acid base approach reported in[10]. UV irradiation degradation tests were performed in device equipped by high-pressure Hg lamp with 40 mW $cm^{-2}$. The temperature of samples during degradation tests was kept constant (40 °C). The wetting properties were studied by means of industrial grade permeability tests consistent with the ISO 9073-8:1995 standard. Chemical composition of deposited films was investigated by means of infrared spectroscopy.

## 3. Results

In the past we have reported on the formation of hydrophobic protective films on paper surfaces to make it resistant against water penetration[11].

A typical spectrum of the discharge created in mixture of nitrogen and $C_4F_8$ is shown in Fig. 1.

The spectrum is plotted in the range 300–500 nm, because above 500 nm only the second spectral order was registered. The spectra consist of the molecular bands of second positive system of nitrogen (C $^3\Pi_u \rightarrow$ B $^3\Pi_g$). In case of octafluorbutane admixture intensive bands of CN violet system

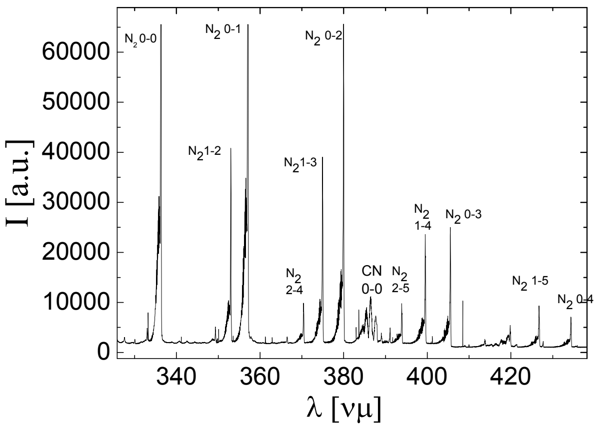


Fig. 1. **Emission spectrum of the surface discharge created in nitrogen with admixture of $C_4F_8$**

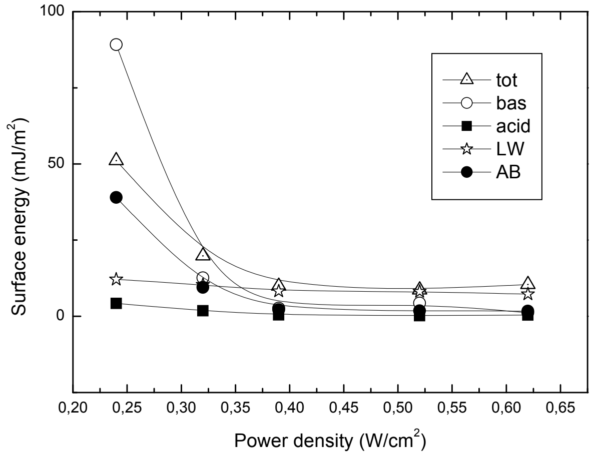


Fig. 3. **Dependence of total surface energy $\gamma^{TOT}$ and its components $\gamma^{LW}$, $\gamma^{AB}$, $\gamma^{+}$, $\gamma^{-}$ plotted as a function of power density**

($^2\Pi \rightarrow {}^2\Sigma$) at 388 nm and 422 nm were observed. The vibrational temperature was calculated from the bands of second positive system of nitrogen ($\Delta v = -2$, heads 0–2, 1–3 and 2–4). The vibrational temperature varied only slightly with discharge power density variation and its estimated value was at about 2100 K in all cases. Fig. 2 shows dependencies of the whiteness W and yellowness Ye of samples in their as-deposited state as a function of the discharge power density.

Solid lines are used as a guide of eyes. Yellowness of the sample increases and whiteness decreases with increasing discharge power density. Sample colour slightly changes, however changes are caused no only by creation of film on the surface but also by thermal and UV degradation of substrate during the deposition process. The electrodes were heated by the discharge and were not cooled with any external cooling system. The electrode temperature was different for different power densities – at higher power density the temperature of electrode was higher.

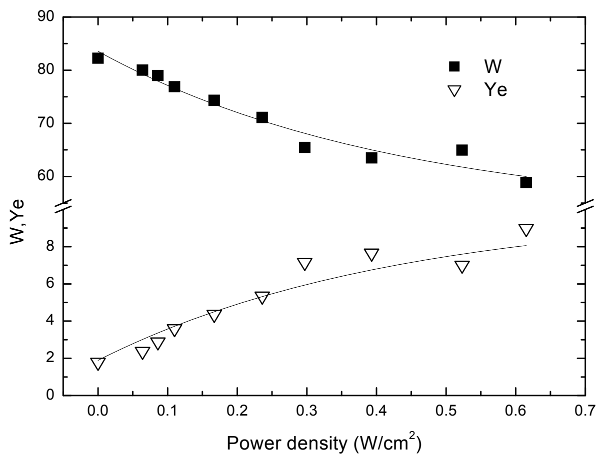


Fig. 2. **Dependence of the whiteness W and yellowness Ye of as deposited samples on the power density. Solid lines represent exponential decrease fit**

In Fig. 3 the dependence of total surface energy $\gamma^{TOT}$ and its components $\gamma^{LW}$, $\gamma^{AB}$, $\gamma^{+}$, $\gamma^{-}$ is plotted as a function of power density. Samples deposited at higher power density then 0.35 W cm$^{-2}$ show similar surface hydrophobic properties, however samples deposited at lower power density exhibit high surface energy.

In these cases surface properties are more in virtue of plasma treatment than deposition of teflon-like surface layer.

The untreated sample is shown as reference and it is rather different then samples after thin film deposition i.e. surface of the untreated sample and sample deposited at the lowest power density is polar, however surface of coated sample is non-polar.

In Fig. 4 the variation of colorimetric parameters under UV irradiation is shown. For degradation test we used high pressure Hg lamp with 40 mW cm$^{-2}$. Whiteness of uncoated samples strongly decreases with increasing UV irradiation time. Samples coated with Teflon-like film exhibit significantly lower degradation than uncoated sample. Samples deposited at lower power densities exhibit less protective properties than samples deposited at higher power densities. Yellowness Ye shows also similar behavior.

## 4. Conclusion

Thin films of highly hydrophobic properties were prepared by means of atmospheric-pressure surface barrier discharge deposition technique. The films were prepared using different power densities from the mixture of octafluorocyclobutane – $C_4F_8$ with nitrogen.

The colorimetric parameters as whiteness and yellowness of samples in their as-deposited and UV irradiated states were studied. The coated samples exhibited considerably higher UV irradiation resistance than the uncoated ones. It is possible to use similar type of films as hydrophobic, transparent and highly effective UV irradiation protective coating on different kind of solids.

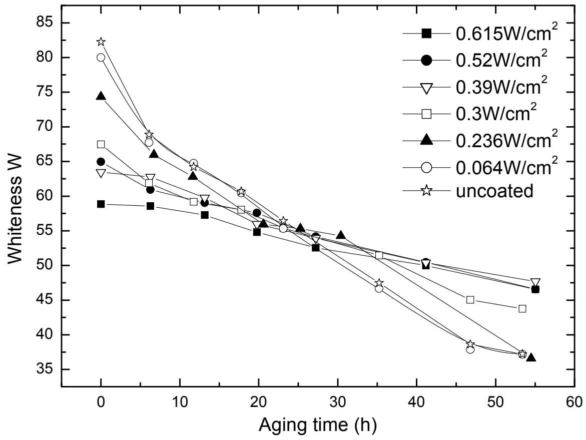


Fig. 4. **Aging effect of samples under UV irradiation. Samples were deposited at different discharge power densities**

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**P. Sťahel, V. Buršíková, J. Čech, Z. Navrátil, and P. Kloc** *(Masarykova Univerzita, Brno, Czech Republic):*
**Deposition and Characterization of Thin Hydrophobic Layers Using Atmospheric-Pressure Surface Barrier Discharge**

The modern technologies often require modification of solid material surfaces with keeping desired bulk properties. To control the surface properties of solids the atmospheric-pressure plasma can be very useful. In this work the thin hydrophobic protective films were deposited on the paper surface using atmospheric-pressure surface barrier discharge. Films were deposited from the mixture of the nitrogen with $C_4F_8$. The plasma properties were investigated by means of optical emission spectroscopy. The properties of samples were investigated by means of colorimetric measurements such as whiteness, yellowness or brightness tests. The surface energy of the thin films was investigated by means of contact angle measurements. The sample properties were measured in as-deposited state and in UV-exposed state.