

THERMAL STABILITY OF SUPERHYDROPHILIC CARBON FILMS

DUGÁČEK Ján¹, DVOŘÁKOVÁ Hana¹, ŠTAHEL Pavel¹

¹CEPLANT - R&D Centre For Low-cost Plasma and Nanotechnology Surface Modifications,
Masaryk University, Brno, Czech Republic, EU

Abstract

Plasma polymerisation in atmospheric pressure is an emerging method of creating highly hydrophilic surfaces, with water contact angles below 10°. Unlike low-pressure plasma polymerisation, it is cheaper, faster and can be done inline, but requires larger amounts of precursor. Unlike plasma activation, the increase of wettability does not show an aging effect. In our experiments, we deposited hydrocarbon films from low concentration propane-butane in nitrogen plasma at atmospheric pressure on c-Si 2 cm x 3 cm large, 0.6 mm thick substrates from distance 0.1 mm. We used three different concentrations of propane-butane. Using thermal desorption spectroscopy, we have systematically analysed the thermal stability of all these films. The samples were slowly heated in high vacuum at constant speed to various temperatures, up to 1000 °C. Thermally desorbed gases from the sample were analysed using a mass spectrometer. The dependences of partial pressures on particle mass and temperature were rendered into colour maps. We have found that reactions begun to occur at temperatures about 100 °C, releasing hydrocarbon gases. Contact angle measurements have shown that the hydrocarbon films progressively lost their hydrophilic effect in temperatures from 100 °C to 300 °C. At temperatures around 850 °C, a strong reaction occurs, leading to a massive release of hydrocarbon gases, but the film itself remains on the substrate. Samples before and after annealing were analysed by means of common laboratory tests.

Keywords: Thermal stability, plasma deposition, superhydrophilic films

1. INTRODUCTION

Polymer thin films with various properties have extensive application in many areas of science and technology. Plasma treatment of surfaces in inert gases or air either modifies the topography of the surface [1] or introduces new functional groups [2]. The disadvantage of this method is the aging effect, gradual loss of improvement of wetting properties due to reactions between the surface and ambient gas [3]. Another disadvantage is strong dependence of reachable wettability on the treated material [4]. These problems can be avoided by using plasma polymerisation [5][6].

Plasma polymerisation is a technique of surface modification that deposits a layer of material polymerised by plasma. The film is usually randomly organised, with short chains and significant crosslinking [7]. This process can be done at atmospheric pressure, which allows fast and continuous processing of surfaces [8].

Determination of their thermal stability at elevated temperatures is crucial for applications where thin film is exposed to higher temperature. In the presented work, we have measured the thermal desorption spectra of samples and learned at which temperatures do reactions occur. We have also measured the wettability after the reactions that occurred during the heating process.

The films were found to be stable at elevated temperatures. Temperatures up to 100 °C inflicted no changes in the wettability of the film, but higher temperatures caused the film's hydrophilicity to deteriorate.

2. EXPERIMENTAL

2.1. Film deposition

Samples were 0.6 mm thick, rectangle shaped with edges 2 cm and 3 cm long. We have used nitrogen with purity 99.9999% was mixed with commercial mixture of propane-butane, consisting of 84% propane, 15% butane and 1% other hydrocarbons. We have created samples at different concentrations of propane-butane, either 0.4%, 0.8%, 1.2% or 0% (no film created, but the surface was treated with plasma). The gas flow was 3 l/min In this atmosphere, the samples were treated for 20 seconds from distance 0.1 mm with diffuse coplanar dielectric barrier discharge (DCSBD) operating at power 400 W (distributed over discharge surface 160 cm² and width 0.3 mm), voltage 20 kV and frequency 15 kHz. Because we were going to heat the sample to high temperature, Czochralski silicon wafers were used as a model substrate. The apparatus used for this experiment can be seen on **Figure 1**.

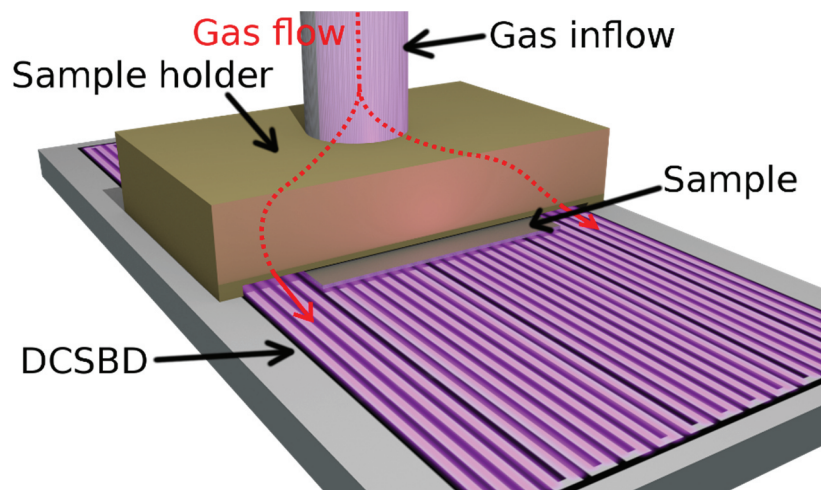


Figure 1 Schematic illustration the apparatus used for deposition

2.2. Thermal desorption

Thermal desorption spectra were measured in a custom built apparatus (as seen on **Figure 2**) that slowly heats the samples, measuring the gases desorbed during chemical and physical reactions in the sample, irreversibly altering it in the process.

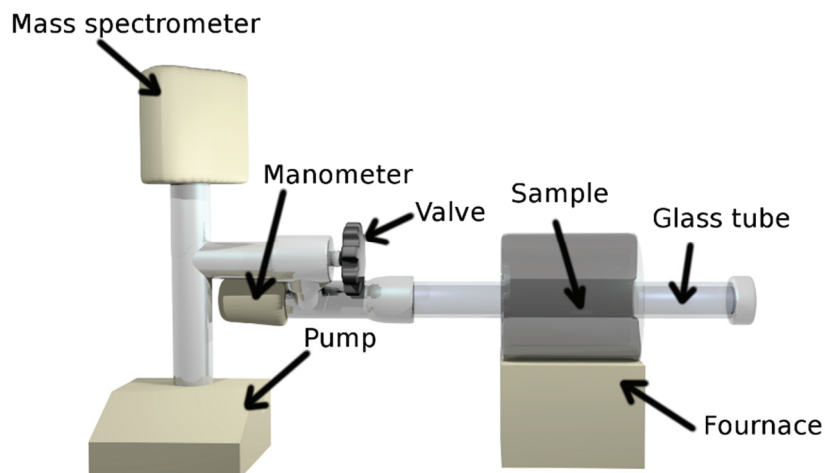


Figure 2 Thermal desorption measurement apparatus

The samples were located in a glass tube evacuated by a Pfeiffer D - 35614 Asslar turbomolecular pump. The glass tube is located in a Clasic 4011T laboratory furnace. The molecular masses of desorbed gases is measured by a Pfeiffer Prisma 80 mass spectrometer.

A problem of this method is desorption of gases from the sample's substrate and from the walls of the apparatus. Because of that, the measurements have to be periodically done with an empty apparatus to determine what is desorbed from the walls. Although the exact partial pressures is difficult to estimate from the measured ion currents and thus the background cannot be simply subtracted, the presence of chemical reactions can be determined qualitatively.

The gas spectrometer's controlling software, TalkStar, only allows measuring either one spectrum at a time or following the development of partial pressures of several molecular masses. We have found a way to work around this limitation.

We have found that if the program is in 'scan' mode, it measures the spectrum continually and while it displays and exports only the latest one, the binary .tds file where it writes the data keeps growing. By making very short measurements containing only several points and exporting them into a readable format, we have found the way the values are stored in this file.

The data are saved in entries of one or more values. Each entry contains the number of its first molecular mass measured encoded as a 32-bit integer (not in any units), the number of measured values in this entry encoded as a 32-bit integer and a series of measured values stored in the IEEE 754 format. The times when these values were measured were not saved, but they could be determined because the measurement speed was constant. The molecular masses measured could be recalculated to arbitrary units by locating the maxima of gases that are always present, like N₂, O₂ or H₂O. A program to decode the files, pair them with temperatures using linear interpolation and plot the results was written in C++.

The results are colour maps where the colour shows the amount desorbed of gas of given mass at given temperature (mass is the x coordinate, temperature is the y coordinate). Because the desorption from other sources than the film cannot be avoided, it must always be compared with data from measurements with empty apparatus.

3. RESULTS AND DISCUSSION

We have measured the spectrum up to 1000 °C of a sample created at 0.4% concentration of propane-butane (**Figures 3, 4**). The heating speed was 5 °C/min. We have found mostly hydrocarbon releases. These were at large ranges of masses, which is typical for hydrocarbons and their fragments. The desorption started at temperatures around 100 °C and increased at higher temperatures. The desorption reactions peaked at temperatures around 850 °C.

We have also found short-term increases of desorption at temperatures 220 °C, 250 °C and 500 °C. These desorption peaks are too short-lasting to possibly correspond to chemical reactions. They most likely came from cracks in the layer that occurred during the heating.

Many of these substances were also released from the background, but at significantly lesser quantities. The short peaks from crack-releases did not occur. The hydrocarbons released were probably leftovers from measurements in which the products of samples' decomposition were adsorbed on the apparatus' walls.

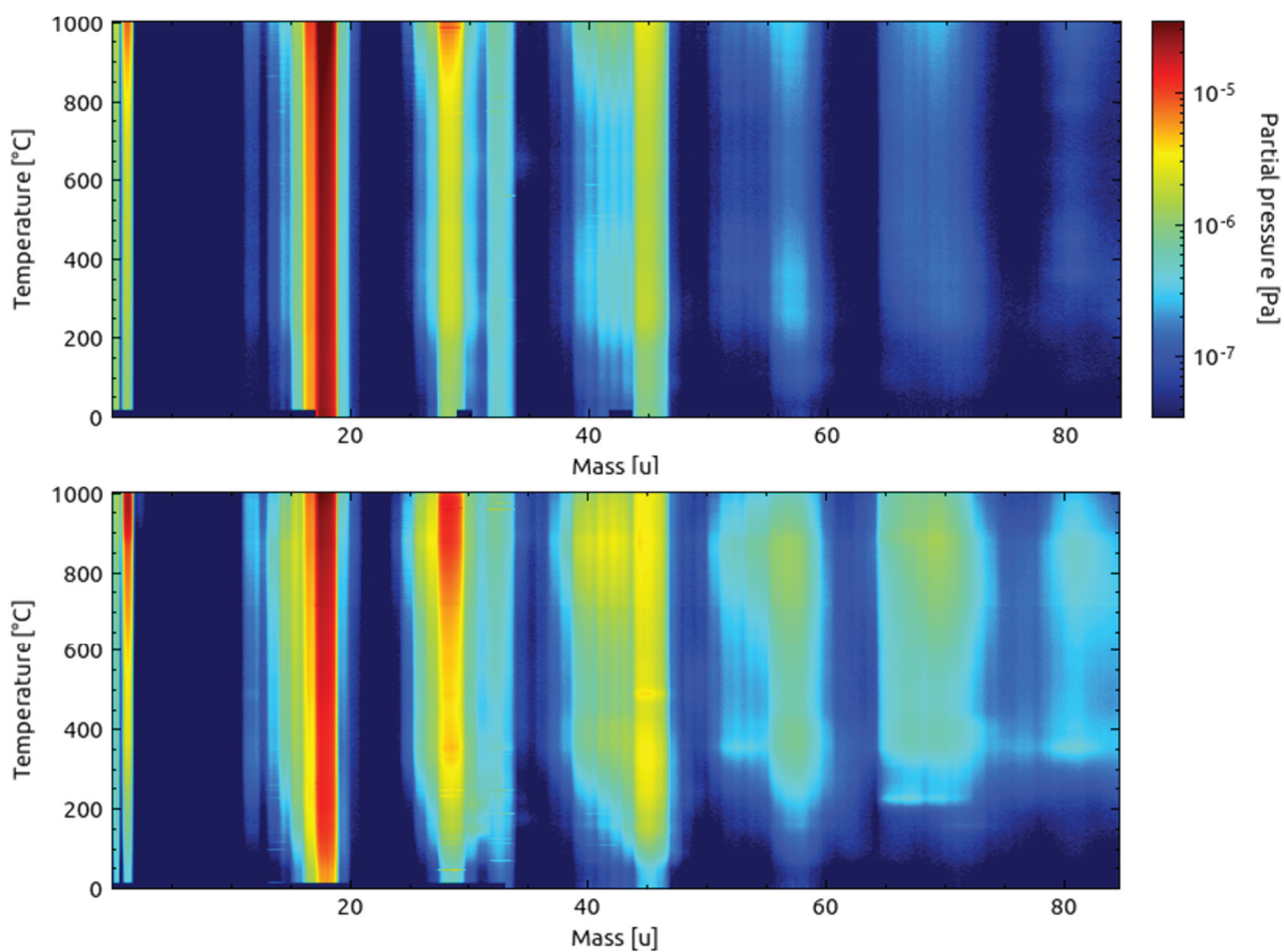


Figure 3 Development of mass spectrum of desorbed gas from the sample created with a 0.035% concentration of propane-butane (lower) compared to sample without film (upper)

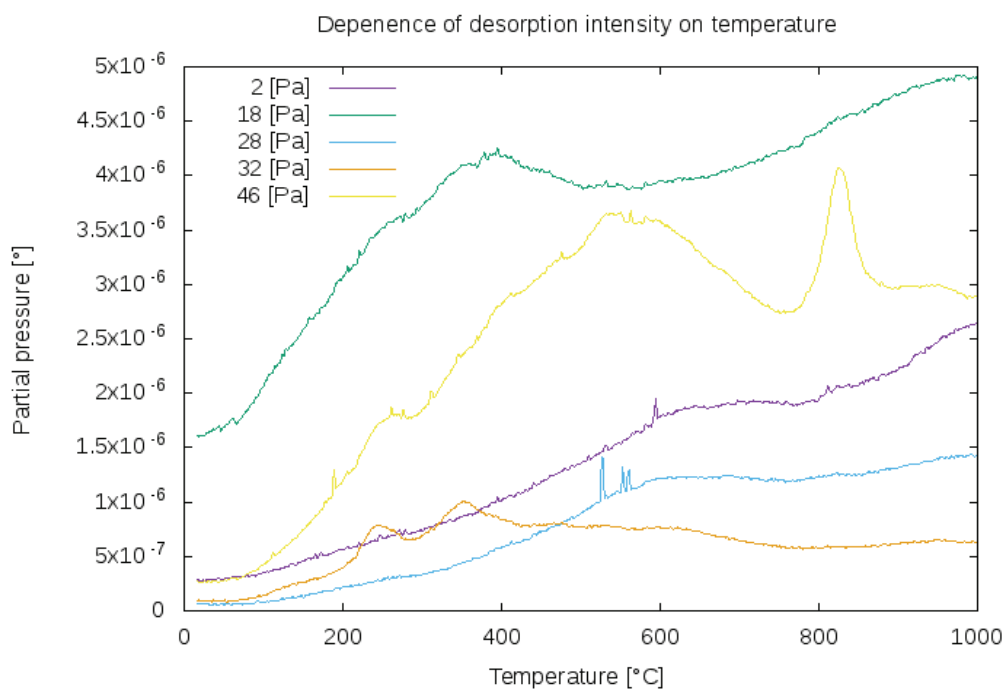


Figure 4 Development of thermal desorption intensity on temperature for selected molecular masses

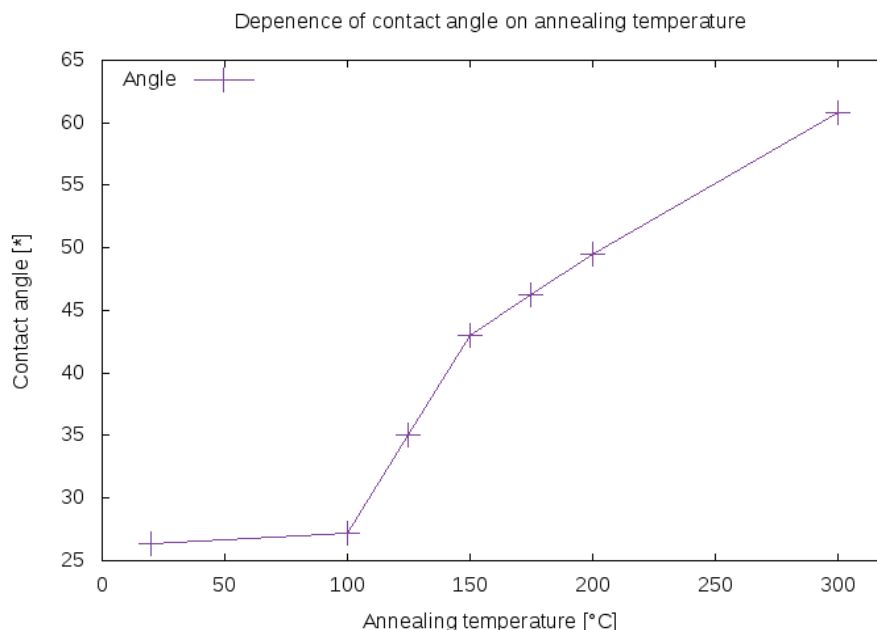


Figure 5 Dependence of surface contact angles after annealing on maximal annealing temperature reached

Next, we compared measured the contact angles of the samples after heating to various temperatures and keeping them on these temperatures for 30 minutes. The results are shown on **Figure 5**. We have found that the contact angle increased with annealing temperature from 26 ° to 60 °. It did not increase further in the range between 300 °C and 1000 °C.

To verify that the decrease in contact angle was not caused by desorption of water adsorbed to the surface, we have tested how the contact angles develop in time while exposed to ambient air humidity. No changes were detected, meaning that the changes are of chemical nature and permanent, consistently with the hydrocarbon releases visible in thermal desorption spectra.

For reference, we have measured the water contact angle of clean silicon substrate was found it was 50 °. This means that the thermally damaged film remains on the surface, but lost its hydrophilic properties.

Despite the changes in the film's composition during annealing to temperatures up to 1000 °C, the film remains visible to naked eye, which is consistent with the observed influence on contact angle.

4. CONCLUSION

We have measured the thermal stability of hydrocarbon films deposited on silicon substrate. The films were created using propane-butane gas in nitrogen plasma. The films were found to be stable until temperature 100 °C, then their properties progressively worsened, losing all the hydrophilic properties before reaching temperature 300 °C. The changes were permanent. A strong reaction occurred at temperature 850°C. Even after annealing to temperature 1000 °C, the film remained on the substrate, albeit devoid of its hydrophilic properties.

REFERENCES

- [1] M. NOESKE, J. DEGENHARDT, S. STRUDTHOFF, U. LOMMATZSCH, Plasma jet treatment of five polymers at atmospheric pressure: surface modifications and the relevance for adhesion, *Int. J. Adhes. Adhes.* 24 (2004) 171-177.

- [2] F. PALUMBO, R. DI MUNDO, D. CAPPELLUTI, R. D'AGOSTINO, SuperHydrophobic and SuperHydrophilic Polycarbonate by Tailoring Chemistry and Nano□texture with Plasma Processing, *Plasma Process. Polym.* 8 (2011) 118-126.
- [3] L. J. GERENSER, XPS studies of in situ plasma-modified polymer surfaces, *J. Adhes. Sci. Technol.* 7 (1993) 1019- 1040.
- [4] J. S. CHO, K. H. KIM, S. HAN, Y. W. BEAG, S. K. KOH, Hydrophilic surface formation on polymers by ion-assisted reaction, *Prog. Org. Coat.* X48 (2003) 251-258.
- [5] M. MALMSTEN, J. Å. JOHANSSON, N. L. BURNS, H. K. YASUDA, Protein adsorption at n-butane plasma polymer surfaces, *Colloid. Surface. B* 6 (1996) 191-199.
- [6] H. DVOŘÁKOVÁ, M. ŠTIPL, J. ČECH, J. JURMANOVÁ, P. ŠTAHEL, Fast low-cost hydrophilisation of surfaces using plasma polymerisation, Hakone XV conference, *Book of Contributed Papers*, 294-296
- [7] H. BIEDERMAN *Plasma polymer films*, Imperial College Press, London, 2004
- [8] F. MASSINES, C. SARRA-BOURNET, F. FANELLI, N. NAUDÉ, N. GHERARDI, Atmospheric pressure low temperature direct plasma technology: status and challenges for thin film deposition, *Plasma Process. Polym.* 9 (2012) 1041-1073.