DEPOSITION OF POLYMER FILMS IN RF DISCHARGE
AT ATMOSPHERIC PRESSURE

1 A. Brablec, 1 Pavel Slavicek, 1 Vratislav Kapicka, 1 Milos Klima, 1 M. Elias,
2 Milos Sicha, 3 D. Slavinska, 3 M. Trchova and 3 H. Biederman

1 Dep. of Phys. Electronics, Faculty of Science, Masaryk University,
Kotlarska 2, 611 37 Brno, Czech Republic
2 Dep. of Electronics and Vacuum Physics, Faculty of Mathematics and Physics,
Charles University, V Holesovickach 2, 18000 Prague, Czech Republic
3 Dep. of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University,
V Holesovickach 2, 18000 Prague, Czech Republic

E-mails: A.Brablec: abr92@velanor.sci.muni.cz, P. Slavicek: px94@sci.mmuo.cz,
V. Kapicka: kapa@velanor.sci.muni.cz, M. Sicha: sicha@mbbox.troja.mff.cuni.cz.

Abstract

RF discharges can burn very well even at atmospheric pressure. Special properties of RF discharges offer many hopeful technological applications like deposition of thin solid films, cleaning and treatment of surfaces, restoration of archaeological artefacts, etc. It was also demonstrated that the discharges could burn under the liquid level. They can interact with the material and then new chemical compounds can arise. Therefore, the detail knowledge of their physical parameters has been required. The parameters of the plasma channel were investigated by spectral and optical methods. In this contribution we report some typical properties of the discharge which has been already studied intensively several years [1-5].

1. Introduction

The described plasma source [1-6] is based on the RF discharge. The advantage of these plasma sources consists in the discharge remains stable up to the atmospheric pressure of the working gas. The discharges can be driven in argon, in air and other gases and they burn both in open space and in liquid environment, too. The discharge can be used for the effective treatment of different objects.

Preliminary results were already presented in Symposium HAKONE VII [8]. Here, we specify more the experiments and add optical diagnostics of plasma.

2. Experimental set-up
The powered RF electrode of the torch discharge plasma source is made from the metal pipe with an inner diameter of 1-2 mm and with a length of several centimetres. The electrode is connected through the matching unit to the RF generator of the frequency of 13.56 MHz. The argon working gas flows through the RF electrode at the nozzle. The argon with an admixture of n-hexane goes directly to discharge. The first gas flow was lower than 900 ccm/min while the second one with n-hexane was 100 ccm/min. The RF power absorbed in the torch discharge has been adjusted in the range from 50 W till 150 W. The length of the discharge was about 3 cm and the discharge has been not connected with the substrate (see Fig.1).

Fig.1. Experimental set-up: 1 - rf generator PG501 at 13.56 MHz, 2 - matching unit, 3 - plasma nozzle, 4 - working gas argon, 5 - flask in which argon bubbles through n-hexane, 6 - glass nozzle, 7 - substrate holder with sample.

Polymer films were deposited on the substrate of Al sheet, Cu substrate polished plates and Si wafers. The thickness of the films was found to be 150 nm as measured by Surfometer SF 10 that allowed to assess surface roughness as 10 nm. The films seem to have good adhesion and they do not peel off in distilled water. Wettability of the films was determined measuring the contact angle of the water droplet (2 mm in DIA) using the home made measuring equipment. From the static measurements when water droplet is dropped on the film surface and left on itself we have found increased wettability as contact angle was 10° for films on Al foils. The contrast very much to the value 60° obtained on Al before deposition. In contrary the films deposited on Cu decreased wettability of this surface and values of the static contact angles before and after deposition were 60° and 85°, respectively. In dynamic mode of measurement at first we increased volume of the water droplet and the advancing contact angle was determined then when reducing volume of the water droplet receding contact angle was found. The difference of the both angles for the film on Al was 27° for the film on Cu it was 61°. The results obtained in the latter case are comparable to plasma polymer films deposited from the mixture Ar/n-hexane/ H2O [7]. Difference of advancing and receding angles is explained by the presence of polar groups that overturn from the film surface in the presence of polar liquid. The occurrence of polar groups is found by FTIR spectroscopy that also revealed a great difference in the structure of films deposited on Al and Cu. The corresponding FTIR absorption is shown in Fig. 2.
The details of these measurements are as follows. The structural and optical properties of the samples were checked using Fourier transform infrared (FTIR) spectroscopy. Infrared measurements were performed on Nicolet IMPACT 400 FTIR spectrometer in an H2O-purged environment. An ambient-temperature deuterated triglycerine sulphate (DTGS) detector was used in the wavelength range from 400 to 4000 cm⁻¹. The Happ-Genzel apodization function was used in the whole region and the spectral resolution was 2 cm⁻¹. Approximately 300 scans were coadded to achieve the signal-to-noise ratio shown. The spectra were corrected for the H2O and CO2 content in the optical path.

First emission VIS spectra were obtained by means of the monochromator HR640, Jobin Yvon (1200 gr/mm, CCD camera Spectrum One).

3. Results

Absorption FTIR spectra obtained by specular reflection on film deposited on Cu polished substrate is given in Fig. 2. The presence of hydrogen in the film is demonstrated by the band of the stretching vibrations of CH groups situated in the region at about 2800-2950 cm⁻¹. The corresponding bands of bending vibrations of CH groups are at about 1460 cm⁻¹. The presence of OH groups associated by hydrogen bonding is manifested by the large band of stretching vibration in the region about 3400 cm⁻¹ and bending vibration at about 1600 cm⁻¹. The sharp maximum at 1588 cm⁻¹ correspond most probably to the stretching vibrations of C=O or C=N groups. A peak at about 2170 cm⁻¹ corresponding to C≡C, C≡N or C=N=O groups can be observed in the spectrum. The band with maximum at about 2000 cm⁻¹ corresponds most probably to the C=C=C stretching vibration. The small peak at about 632 cm⁻¹ well observed in the spectrum corresponds probably to the symmetric deformation vibration of NO₂ group in secondary nitroalkanes. The groups observed in the FTIR spectrum show that oxygen, hydrogen and nitrogen are chemically incorporated into the film structure.

![Absorbance, a.u.](image)

**Fig. 2:** Absorption infrared spectrum of CH films deposited on a) Al substrate, b) Cu substrate.

Optical emission spectra for two spectral ranges presented in Fig. 3 - 4 show that in pure argon we observe only argon lines and nitrogen bands while in the mixture of argon and n-hexane the molecular bands of CN and C₂ (also argon lines), which originates from molecular n-hexane.
Fig. 3. Optical emission spectra of the discharge burning in pure argon and argon with n-hexane. In the first case we observed molecular band of N_2, second positive system, C^0Π_u - B^2Π_g. In the second case we observed molecular band of CN, violet system, B^2Σ−X^2Σ.

Fig. 4. Optical emission spectra of the discharge burning in pure argon and argon with n-hexane. In the second case we observed molecular band of C_2, Swan system A^3Π_g − X^3Π_u.

4. Conclusion

The presented results show that RF discharges in atmospheric pressure is suitable for plasmachemical and technological processes. Namely, in this moment we conclude that to
prepare thin films is less expensive and easier at atmospheric pressure than at low one. However, the properties of the films have been not so high then we expect.

Acknowledgement

We are grateful to the Grant Agency of Czech Republic for financial support under the contract No 202/99/0305, No 202/01/P017, No 202/00/0843.

References
