

ROLL-TO-ROLL SURFACE ETCHING OF POLYMERS USING HYDROGEN PLASMA AT ATMOSPHERIC PRESSURE

KRUMPOLEC Richard, ZEMÁNEK Miroslav, TUČEKOVÁ Zlata, KELAR Jakub

*R&D Center for Low-Cost Plasma and Nanotechnology Surface Modifications (CEPLANT),
Department of Physical Electronics, Faculty of Science, Masaryk University, Brno,
Czech Republic, EU*

Abstract

This paper reports on plasma surface etching of three different polymers using a low-temperature (80°C) atmospheric-pressure plasma generated in pure hydrogen by a diffuse coplanar surface barrier discharge. Flexible polymer foils were plasma-modified in roll-to-roll configuration. Three polymers, polyethylene naphthalate (PEN), polyethylene terephthalate (PET), and polyimide (PI) foils were exhibited to the hydrogen plasma etching. Scanning electron microscopy was used to determine the change in the thickness of the samples from the measurement of cross-section images of polymer foils. As shown, the etching rate of tested samples was of the order of ~10-100 nm.min⁻¹. Therefore, the presented method is suitable for precise etching of nanostructures and thin polymer film or flexible polymer substrates.

Keywords: Plasma etching, DCSBD, hydrogen, polymers, atmospheric pressure

1. INTRODUCTION

Dielectric barrier discharges (DBDs) are well known as a source of non-isothermal, low-temperature plasma. They are often used for plasma generation at atmospheric pressure in a wide range of gases like ambient air, nitrogen, oxygen, helium, argon and its mixtures. DBDs and generated plasma are successfully utilized for plasma cleaning, activation, functionalization and other modification of various materials and its surfaces. However, atmospheric pressure plasma generated by DBD can also be used for plasma-enhanced chemical vapour deposition (PECVD) of thin films, deposition of complex functional thin films, for plasma etching and creating nanostructured surfaces. The application range of plasma generated by DBDs is vast: from surface engineering, production of nanomaterials to applications in medicine and biology.

Oxidation reactions initiated by DBD plasma generated in an oxidative atmosphere (ambient air, oxygen, etc.) are well known and studied in innumerable publications and found in many real applications [1,2]. However, DBD plasma can be generated also in argon and hydrogen, leaving the possibility to initiate the chemical reduction reactions. Prysiashnyi et al. [3] showed that atmospheric pressure DCSBD plasma can be used for chemical reduction of a native surface CuO/CuO₂ layer. Krumpolec et al. [4] reported hydrogen plasma etching of SiO₂/Si films.

This paper presents a method for atmospheric pressure plasma surface etching of polymers in pure hydrogen plasma generated by a diffuse coplanar surface barrier discharge. Plasma etching was tested at three polymers (PEN, PET, PI). All of them are considered to be a key plastic substrates for future flexible electronics [5,6]. The etching of polymer materials was studied by scanning electron microscopy, and chemical reduction of plasma modified surfaces was analyzed by x-ray photoelectron spectroscopy.

Plasma is a complex mixture of electrons, ion, radicals, molecules and excited species. The interaction of this mixture of active species with materials, especially with polymers, led to the complex reactions leading to the change of surface properties of the substrate. The interactions of species with the surface during plasma etching is either physical or chemical; then the process is called reactive plasma etching or plasma-chemical

etching, respectively. A comprehensive summary of plasma etching of polymers and polymeric materials can be found in a review of Puliyalil and Cvelbar [7]. Kwon et al. [8] used hydrogen plasma sintering process at temperature 150 °C for reduction and densification of copper complex ink. Palmer et al. [9] used a hydrogen-argon thermal plasma (50% H₂ - 50% Ar) for reduction of TiO₂. Selective etching of graphene and graphene nanoribbons using hydrogen plasma reaction at 300 °C was studied by Liming et al. [10]. Hydrogen plasma was also used for surface modification of polymers, e.g. PTFE [11], and plasma etching of PP, PET, PEN, PEEK, PMMA, PLA, LDPE and Nylon 6,6 [12].

2. EXPERIMENTAL

Polyethylene naphthalate (PEN), Polyethylene terephthalate (PET) and Polyimide (PI) polymer foils were used as a substrate for plasma etching. PEN and PET substrates were used as pure polymer foils. A Nikaflex F 30 VC1 foil (Nikkan Industries Co., Ltd.) was used as a polyimide sample, which is used as a substrate for flexible printed circuits. The samples were used as-received, without chemical cleaning, just upper protector was removed from the surface and dust was removed using compressed air.

Plasma etching of small experimental samples was done in a sealed chamber designed to generate the plasma in pure hydrogen. The reactor chamber is described in [4]. The plasma was generated in pure hydrogen (purity 4.8) working gas at atmospheric pressure by diffuse coplanar surface barrier discharge DCSBD (Roplass, Czech Rep.). Power input into DCSBD was 100 W giving the power density in the plasma 2.5 W.cm⁻². The samples were moved at a small constant velocity during the treatment to ensure homogeneous etching. A surface-to-surface distance of sample surface from DCSBD unit was 0.2 mm.

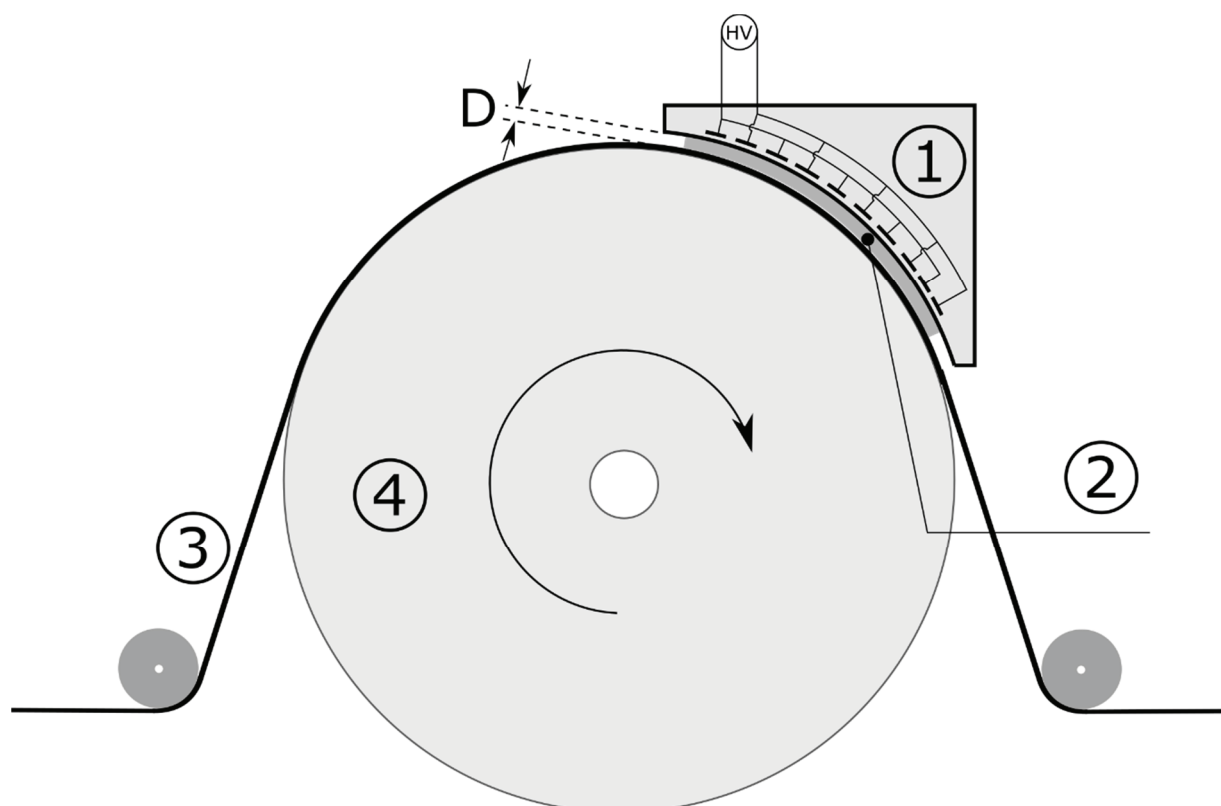


Figure 1 Scheme of roll-to-roll reactor based on DCSBD for plasma etching of flexible substrates: (1) curved-DCSBD unit, (2) low-temperature pure hydrogen plasma generated at atmospheric pressure, (3) polymer foil sample guided by dielectric roller (4)

Large polymer sheets were treated using a reactor designed for roll-to-roll treatment and based on DCSBD with curved alumina ceramic as shown in **Figure 1**. The modified curved-DCSBD unit (1), with curvature $1/14.8 \text{ cm}^{-1}$, generated homogeneous large-area plasma (2) of the same properties as planar-DCSBD configuration. The polymer foil (3) were guided by dielectric roller (4) with a diameter 296 mm at a precise distance D from the plasma. The whole system was closed in a sealed chamber connected to the inlet and outlet gas distribution system.

The experiment was carried out as follows: Prior the etching in pure hydrogen, the gas chamber was purged by pure nitrogen flow (purity 4.8) for several minutes to establish safe and clean conditions before the experiment. Then pure hydrogen flow was established at a specified flow rate for a particular reactor, and the chamber was again flushed for several minutes before plasma was turned on. The chamber was again purged with pure nitrogen after the experiment prior safe opening of the reactor lid. The reaction temperature during the plasma etching was about 80°C .

The changes in surface morphology and etching rate measurement were done by scanning electron microscopy using MIRA 3 device (TESCAN, Czech Republic). All micrographs of samples were taken using the accelerating voltage 10 kV, edge of the samples was observed at accelerating voltage 30 kV. Before the SEM analysis, all samples were coated by a 10-nm layer of Au-Pd composite.

The changes in surface chemistry on plasma modified polymers were studied by means of a high-resolution XPS (X-ray Photoelectron Spectroscopy) performed with the XPS spectrometer ESCALAB 250 Xi (Thermo Fisher Scientific Inc., UK). The system is equipped with 500 mm Rowland circle monochromator with microfocused Al K α X-Ray source. The survey spectra were acquired with a pass energy of 50 eV and resolution of 1 eV. The photoelectron spectra were referenced to the peak of aliphatic C-C bonds at 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software. The transfer time between opening the plasma reactor, manipulation and insertion of the samples into the XPS load-lock chamber was less than 15 min.

3. RESULTS AND DISCUSSION

PEN, PET and PI flexible polymer foils were etched in the pure hydrogen plasma for 60 min. The thickness of each sample was measured before and after the plasma etching and etching rate was calculated from the reduction of the thickness. **Figure 2** shows SEM micrographs of cross-sectional images of PEN (a), PET (b) and PI (c) before and after plasma etching.

Table 1 shows measured sample thickness before and after 60-min plasma etching with a calculated etching rate of each sample. The measured etching rate of PI, PET and PEN was $83 \text{ nm}\cdot\text{min}^{-1}$, $175 \text{ nm}\cdot\text{min}^{-1}$ and $200 \text{ nm}\cdot\text{min}^{-1}$, respectively.

Table 1 Measured thickness of the samples before and after plasma etching

Sample	Thickness (μm)		Difference (μm)	Etching Rate ($\text{nm}\cdot\text{min}^{-1}$)
	before	after		
PEN	130 +/- 1	117.5 +/- 5	-12	200
PET	30 +/- 1	19.3 +/- 1	-10.5	175
PI	50 +/- 0.65	45 +/- 1	-5	83

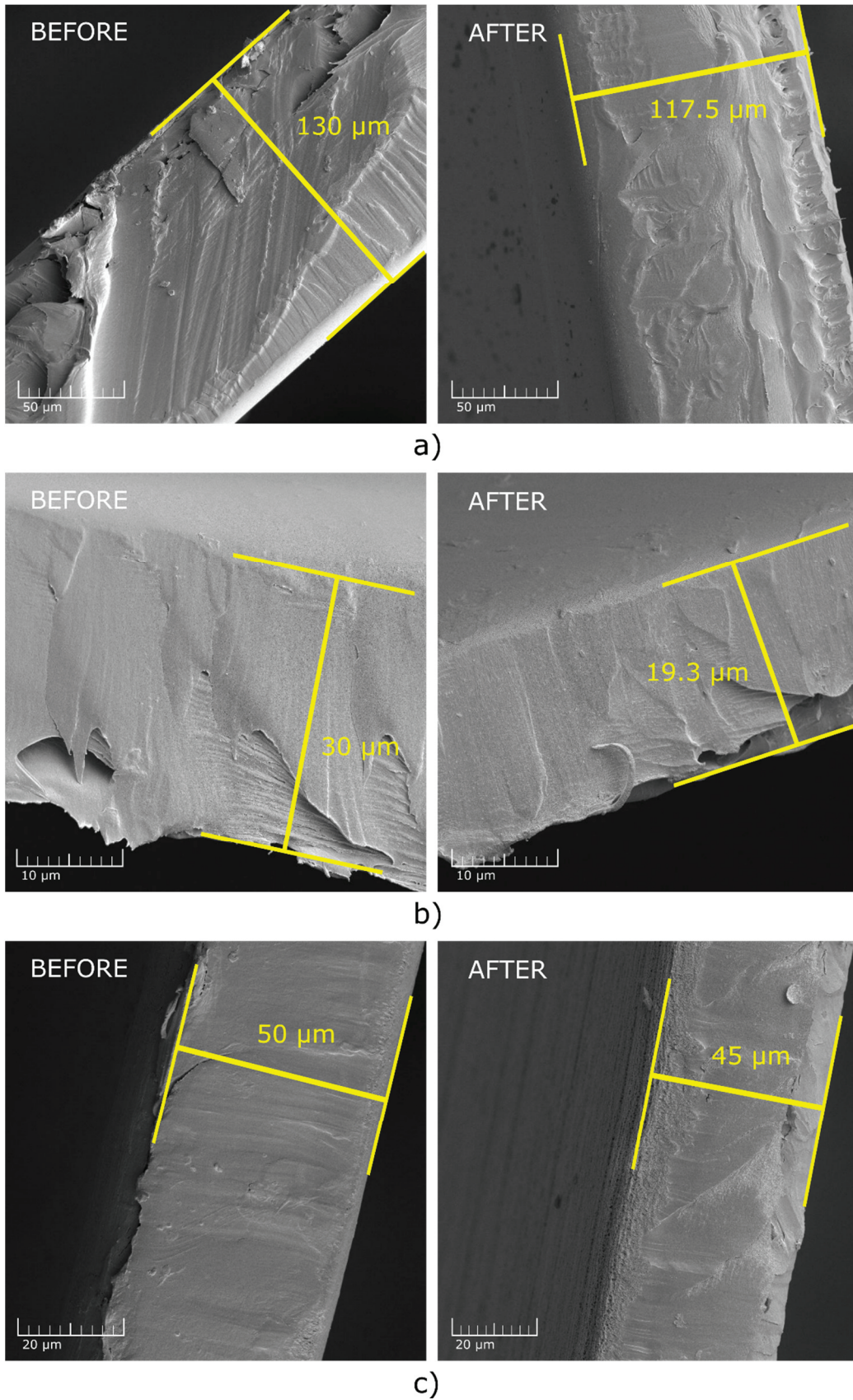


Figure 2 SEM micrographs of PEN (a), PET (b) and PI (c) before and after 60-min plasma etching in pure hydrogen plasma

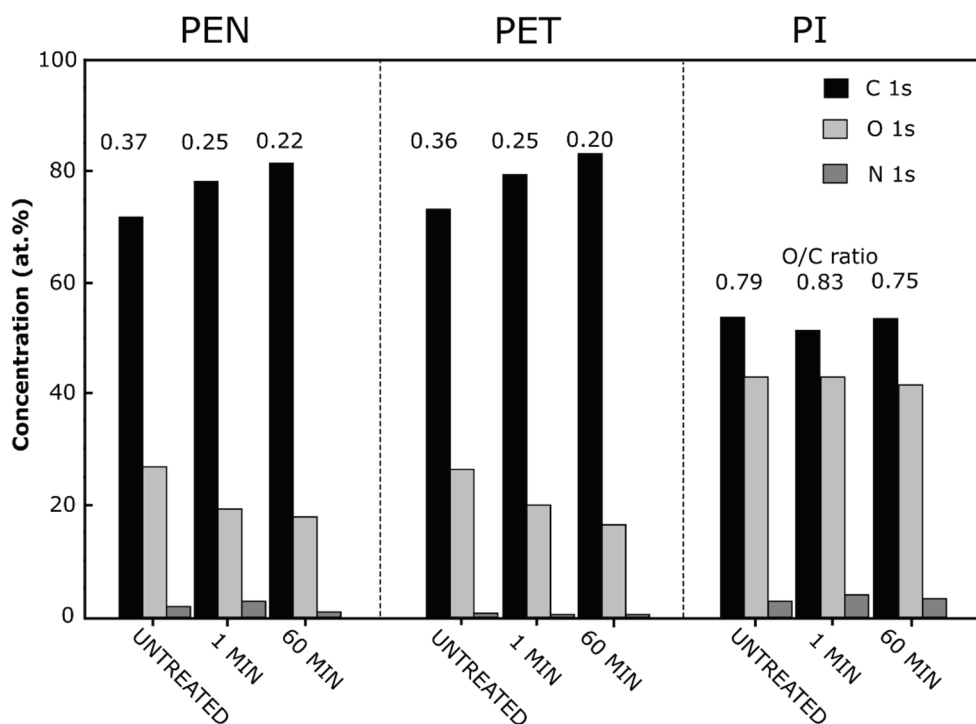


Figure 3 Concentration of elements on PEN, PET and PI before and after plasma etching in H₂ plasma with O/C ratio values (column labels)

Surface chemical analysis performed by XPS revealed a different effect of reduction hydrogen plasma on etched polymer samples (**Figure 3**). In case of PEN and PET samples, the surface was fast reduced. Even 1-minute plasma treatment led to a decrease of oxygen concentration to 19 at.% from reference value 27 at.% on PEN sample. On PET, oxygen concentration decreased to 20 at.% from reference value 26 at.%. Long 60-min etching led to the further decrease of oxygen concentration to 18 at.% on PEN and 16 at. % on PET foil. Oxygen-to-carbon ratio was decreased after the plasma etching by 42 % on PEN sample at value O/C = 0.22 from starting value 0.37 measured on untreated sample. On PET, oxygen-to-carbon ratio decreased by 46 % to value about 0.20 from ratio O/C = 0.36 on untreated sample.

On the other hand, plasma etching of PI samples is slower. 60-s etching of PI led to the no change in oxygen concentration, and even 60-min etching led to a small decrease of oxygen concentration to 40 at.% from the value 43 at.% measured on untreated sample. Oxygen-to-carbon ratio decreased after 60-min etching only by 5 %. A small increase of O/C ratio by 5 % after the first 60-sec etching is probably the result of very slow etching & reduction reactions of hydrogen plasma on PI resulting in small changes of C, O and N concentrations on plasma treated sample. No significant change in nitrogen concentration was observed after the etching.

Despite the preliminary results obtained in this work, it is evident that atmospheric-pressure hydrogen plasma is capable of being a promising method for surface etching of polymers or thin polymeric films. Based on observed etching rates in the order of ten to hundreds of nanometers per minute, the method is suitable for precise etching of thin nanoscale polymer films. It was reported, that diffuse coplanar surface barrier discharge in hydrogen gas generates stable, high power and high electron density ($n_e = (1.3 \pm 0.1) \times 10^{16} \text{ cm}^{-3}$) plasma with a mean electron temperature of about $T_e = (19 \pm 3) \times 10^3 \text{ K}$ [3]. However, more research is needed to reveal the precise reaction mechanism of hydrogen plasma with the surface of polymeric materials. The presented method successfully utilizes a roll-to-roll, low-temperature, hydrogen plasma for plasma etching of polymeric flexible foils which become more and more important substrates for future technologies.

4. CONCLUSION

Pure hydrogen DCSBD plasma was used to etch the surface three different polymer films. Etching of surface polymer film was confirmed by SEM cross-section analysis. The measured etching rate of PI, PET and PEN was $83 \text{ nm}\cdot\text{min}^{-1}$, $175 \text{ nm}\cdot\text{min}^{-1}$ and $200 \text{ nm}\cdot\text{min}^{-1}$, correspondingly. Surface chemical analysis performed by XPS revealed different behaviour of reduction plasma on etched polymer samples. In case of PEN and PET samples, the surface was fast reduced leading to a decrease of oxygen concentration to 19 at.% from reference value 27 at.% on PEN and to a decrease of oxygen concentration to 20 at.% from reference value 26 at.% on PET after 1-min exposure in pure H_2 plasma. Longer etching led to the further decrease of oxygen concentration. On the other hand, plasma etching of PI samples was slower. 60-s etching of PI led to the no change in oxygen concentration, and even 60-min etching led to the decrease of oxygen concentration to 40 at.% from value of 43 at.% measured on untreated sample. Etching is besides the films deposition an important production step in microelectronics, which tends a big move to flexible polymer substrates from standard silicon wafers. As revealed, low-temperature ($80 \text{ }^\circ\text{C}$) plasma treatment in pure hydrogen plasma can be used for precise etching of polymers. The presented method of roll-to-roll plasma etching could be a new way of plasma processing of flexible polymer foils.

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support from project LO1411 (NPU I), funded by Ministry of Education, Youth and Sports of the Czech Republic. The authors also thank to Dr. Monika Stupavská for acquiring the XPS data.

REFERENCES

- [1] BORCIA, G. et al. The surface oxidation of selected polymers using an atmospheric pressure air dielectric barrier discharge. Part II. *Applied Surface Science*, 2004, vol. 225, no. 1-4, pp. 186-197.
- [2] JELILI, R. A. A review of low-temperature plasma treatment of textile materials, *Journal of Materials Science*, 2015, vol. 50, pp. 5913-5943.
- [3] PRYSIAZHNYI, V. et al. Generation of Large-Area Highly-Nonequilibrium Plasma in Pure Hydrogen at Atmospheric Pressure, *Contribution to Plasma Physics*, 2014, vol. 54, pp. 138-144.
- [4] KRUMPOLEC, R. et al. Atmospheric pressure plasma etching of silicon dioxide using diffuse coplanar surface barrier discharge generated in pure hydrogen, *Surface and Coatings Technology*, 2017, vol. 309, pp. 301-308.
- [5] NATHAN, A. et al. Flexible electronics: The next ubiquitous platform, *Proceedings of the IEEE*, 2012, vol. 100, pp. 1486-1517.
- [6] KIM, K. N. et al. Atmospheric pressure plasmas for surface modification of flexible and printed electronic devices: A review. *Thin Solid Films*, vol. 598, pp. 315-334.
- [7] PULIYALIL, H., CVELBAR, U. Selective Plasma Etching of Polymeric Substrates for Advanced Applications, *Nanomaterials*, 2016, vol. 6, no.6, pp. 108.
- [8] KWON, Y.-T. et al. Full densification of inkjet-printed copper conductive tracks on a flexible substrate utilizing a hydrogen plasma sintering, *Applied Surface Science*, 2016, vol. 396, pp. 1239-1244.
- [9] PALMER, R. A. et al. Reduction of TiO_2 with Hydrogen Plasma, *Plasma Chemistry and Plasma Processing*, 2002, vol. 22, no. 3, pp. 335-350.
- [10] XIE, L., JIAO, L., DAI, H. Selective Etching of Graphene Edges by Hydrogen Plasma, *Journal of American Chemical Society*, 2010, vol. 132, pp. 14751-14753.
- [11] INAGAKI, N., TASAKA, S., UMEHARA, T. Effects of Surface Modification by Remote Hydrogen Plasma on Adhesion in Poly(tetrafluoroethylene)/Copper Composites, *Journal of Applied Polymer Science*, 1999, vol. 71, pp. 3-5.
- [12] KUZMINOVA, A. et al., Etching of polymers, proteins and bacterial spores by atmospheric pressure DBD plasma in air, *Journal of Physics D: Applied Physics*, 2017, vol. 50 pp. 11.