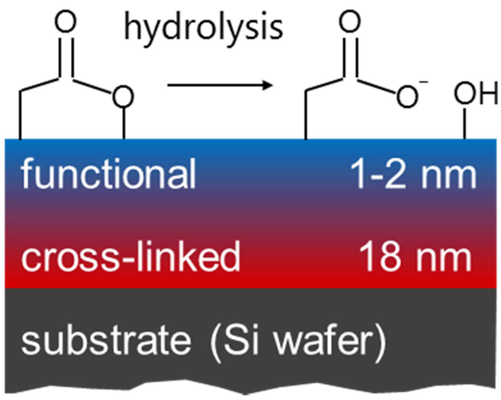
Reduced aging phenomena in graded plasma polymer films

Patrick Rupper[1], Marianne Vandenbossche[1], Laetitia Bernard[2], Dirk Hegemann[1], Manfred Heuberger[1]

[1]Laboratory for Advanced Fibers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St.Gallen, Switzerland
[2]Laboratory for Nanoscale Materials Science, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland
patrick.rupper@empa.ch

Plasma polymer films (PPFs) are known for their enhanced stability compared to conventional polymer coatings. However, the usage of highly functional PPFs is often limited by aging phenomena in air or in aqueous environments due to oxidation, hydrophobic recovery, hydrolysis and dissolution of oligomeric fragments [1,2]. It is possible to enhance the stability of PPFs by increasing the cross-linking degree at the cost of the terminal functional groups, but those are needed for different biomedical applications such as biosensors and tissue-engineered implants.



An advanced strategy for creating stable yet functional PPFs is presented which is based on a vertical structural and chemical gradient implemented in the PPFs [3,4,5]. This vertical gradient is composed of a highly cross-linked subsurface structure, gradually changing into a more functional nanoscaled surface termination layer (see Figure). The gradient layer was achieved using discharges in gaseous mixtures with decreasing power input and increasing gas ratio during plasma polymer deposition. Aging behavior and stability was studied in air and in different aqueous environments using complementary characterization methods including angle-resolved X-ray photoelectron spectroscopy (ARXPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Simple models for the oxygen depth distributions were studied. A fast hydrophobic recovery, followed by midterm radical reactions and progressive hydrolysis reactions under non-neutral pH conditions were identified.

Compared to homogeneous plasma polymer structures, it was found that in air and in neutral water, the gradient films are stabilized over a period of at least one week. Changes in the oxygen depth profiles have been observed at pH 4 and pH 10 showing structural and chemical aging effects on different time scales. The use of vertical gradient plasma polymer nanofilms represents a novel approach to reduce aging mechanisms and/or to provide time-controlled degradable PPFs which have a high potential regarding applications in drug release or non-fouling surfaces.

References:
[1] Sufal Swaraj, Umut Oran, Andreas Lippitz, Jörg F. Friedrich, Wolfgang E. S. Unger, Plasma Process. Polym. **4**, S784 (2007).
[2] Martin Drabik, Jaroslav Kousal, Coralie Celma, Patrick Rupper, Hynek Biederman, Dirk Hegemann, Plasma Process. Polym. **11**, 496 (2014).
[3] Patrick Rupper, Marianne Vandenbossche, Laetitia Bernard, Dirk Hegemann, Manfred Heuberger, Langmuir **33**, 2340 (2017).
[4] Johanna Dorst, Marianne Vandenbossche, Martin Amberg, Laetitia Bernard, Patrick Rupper, Klaus-Dieter Weltmann, Katja Fricke, Dirk Hegemann, Langmuir **33**, 10736 (2017).
[5] Marianne Vandenbossche, Dirk Hegemann, Curr. Opin. Solid State Mater. Sci., in press (2018).