# Plasma chemical gas phase processes in plasma polymerization

D. Hegemann[1], B. Hanselmann[1], R. Deradjat[1,2], M. Drabik[1]

[1]*Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St.Gallen, Switzerland*

[2]*Ruhr University Bochum, Institute for Theoretical Electrical Engineering, 44801 Bochum, Germany*

The plasma chemical reaction pathway yielding plasma polymer growth consists of multistep reactions taking part in the gas phase and at the surface. New insights are gained by comparing mass deposition rates under varying energetic conditions with optical emission spectrometry.

## 1. Introduction

Plasma polymerization is activated by electron excitation in the gas phase yielding different fragments of different numbers and reactivities [1]. Further steps finally yielding film growth might involve plasma chemical gas phase reactions and reactions at the growing film surface. Considering the number of collisions in the gas phase and energetically favourable reactions at the surface, it appears reasonable to assume that most chemical reactions are taking place at the surface [2]. Plasma diagnostic methods such as mass spectrometry (MS) and optical emission spectrometry (OES) tend to observe (stable) species that do not contribute to film growth.

## 2. Approach

### 2.1. Macroscopic kinetics

In order to gain more insights into plasma polymerization processes, we therefore developed a (macroscopic) concept based on the energy input both into the gas phase (plasma) and during film growth (surface) that helps to distinguish between predominating gas phase or surface processes [3].

A well-defined reactor geometry was used allowing reliable plasma conditions over a broad parameter range concerning power input *W* and gas flow *F*. By measuring excitation voltage of the RF discharge and electron density, the mean ion energy and the ion flux incident at the substrate surface can be estimated yielding the energy density deposited into the growing film, i.e. the energy flux per deposition rate [4]. Moderate energy densities induce crosslinking, while higher values promote ion-induced effects such as etching.

### 2.2. Results

Typically, an increase in (mass) deposition rate is obtained by increasing the reaction parameter *W*/*F*, which shows quasi-Arrhenius behavior, followed by a drop in film growth at higher specific energy input. To analyze plasma chemical and physical influences, different experimental series using gas mixtures of $CO_2/C_2H_4$ were performed at different gas flows. Thereby, the same range of *W*/*F* can be maintained at different energy flux to the substrate. As a result it was obtained that $CO_2/C_2H_4$ discharges show a transition that is dominated by plasma chemical processes (Fig. 1).

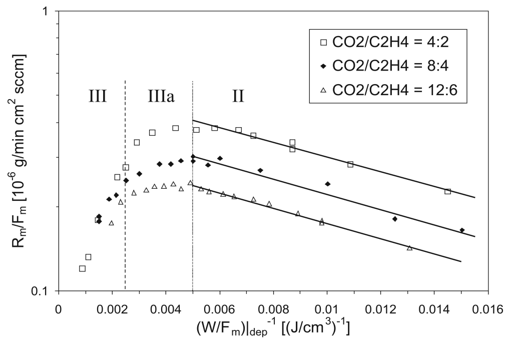


Fig. 1: *The change in deposition rate in regime IIIa is caused by a change in the plasma chemical reaction pathway, since it occurs at fixed W/F independent of the different ion bombardment conditions.*

Using OES, it was investigated whether this transition is accompanied by a change in the gas phase composition of reactive species such as CO, O, H and, CH.

## References

[1] D. Hegemann, E. Körner, S. Chang, J. Benedikt, A. von Keudell: Appl. Phys. Lett. 100 (2012), 051601.

[2] O. Gabriel, D.C. Schram, R. Engeln: Phys. Rev. E 78 (2007), 016407.

[3] D. Hegemann, E. Körner, K. Albrecht, U. Schütz, S. Guimond: Plasma Process. Polym. 7 (2010), 889.

[4] D. Hegemann, U. Schütz, E. Körner: Plasma Process. Polym. 8 (2011), 689.