Influence of Gas Phase and Surface Reactions on Plasma Polymerization

Dirk Hegemann\textsuperscript{1}, Enrico Körner\textsuperscript{1}, Sebastien Guimond\textsuperscript{1}

\textsuperscript{1}Empa, St.Gallen, Switzerland
dirk.hegemann@empa.ch

The formation of plasma polymers is based on multistep reactions that are taking place both in the gas phase and on the surface. In order to gain more insights and to control plasma polymerization processes, some assumptions can be made that allow a macroscopic approach. Therefore, a concept was developed 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.

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 arriving at the substrate surface can be estimated yielding the energy density deposited into the growing film, i.e. ion energy times ion flux per deposition rate. The energy density is mainly a function of $W$. Moderate energy densities induce crosslinking, while higher values promote ion-induced effects such as etching. The energy input into the gas phase, on the other hand, is governed by the reaction parameter $W/F$ (specific energy), where the plasma zone is the source for the film-forming species (concept of chemical quasi-equilibria).

Typically, an increase in deposition rate is obtained with increasing $W/F$, 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 $C_2H_4$ with $CO_2$ or $N_2$ were performed at different gas flows. Thereby, the same range of $W/F$ can be maintained at different ion bombardment to the substrate. As a result it was obtained that $CO_2/C_2H_4$ discharges are dominated by plasma chemical processes, while the drop in deposition rate for $N_2/C_2H_4$ is influenced by the energy density on the surface. These results are used to optimize the permanency of functional plasma polymer films on flexible substrates.

Keywords
RF plasma
energy input
plasma chemistry
functional coating