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Supplementary Material: Fluoropolymer Film Formation by Electron Activated Vacuum Deposition

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A Comparison of Backgrounds of Plasma Discharge in Organic Gas and EVD

At first, to ignite a plasma, it is necessary to produce charge carriers by a gas electrical breakthrough, freeing electrons and ions by the destruction of gas molecules. Energetic species of plasma destroy molecules in the gas phase and on the surface. These partially destroyed molecules acquire free bonds and becoming able to react with another molecule. Active molecules react with each other to produce larger molecules, but no plasma action is required at this stage. To what extent is the growing molecule big? As has been accepted in many papers concerning the classic plasma deposition of organic films, the film structure is a 3-dimensional collection of different groups in a non-repetitive manner. Therefore, film produced by plasma is not possible to call a "polymer". Plasma does not polymerize molecules and the term "plasma polymerization" is not correct from both the gas phase processes and film structure points. Even a special name "plasma polymer" is not correct due to the absence of repeated units in film. Using special kinds of plasma like pulsed ones or depositing film in an afterglow zone from molecules able to react with a chain polymerization mechanism the film with repeated units like in a classic polymer can be produced.

The films produced in classic low temperature self-sustained plasma from any fluorinated gas should be named, for example, "fluorocarbon film with irregular structure and *high molecular mass*". The term "plasma activation" should be used instead of "plasma polymerization" as a correct reflection of physical backgrounds of the all processes.

EVD. Evaporation, i.e. transmission to the gas phase of the whole polymer molecule is not possible, so the term "polymer evaporation" is not correct. The film formation is due to a polymer chain decomposition, evaporation of its fragments, their condensation on a cold surface and secondary polymerization. The deposition is carried out at a low gas pressure. The mean free path of the gas molecules is bigger than the distance between evaporator and surface. Therefore the fragments have no collisions in a gas phase and film is growing on a substrate only without any energetic action. The collisions of injected electrons with fragments in a high vacuum are also limited due to their concentration between a cathode and crucible. The damage of evaporated fragments is expected to be significantly smaller than in classic plasma. The RF plasma in gaseous fragments mediums is igniting due to injected electrons during EVD. The secondary activation of fragments also have to be significantly smaller, than in classic plasma, but bigger, than during EVD. Usage of low RF power for plasma ignition is not limited due to the initial breakthrough of gas being absent. The elevation of pressure to 10^{-3} bar and RF power increase lead to the formation of films like classic plasma deposits.

The inclusion of nitrogen and oxygen at a pressure of residue gasses 10^{-5} bar in the growing film is not possible. The reaction of oxygen with free radicals in the film is possible in air, but to a smaller extent, than in plasma films. The reaction of nitrogen at room temperature with film is not possible.

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