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Study of the transition between capacitive and inductive modes on propanethiol plasma polymer properties: correlation between plasma and film chemistry

Damien Thiry[1], Nikolay Britun[2], Stephanos Konstantinidis[2], Jean-Pierre Dauchot[2], Maxime Guillaume[3], Jérôme Cornil[3], Rony Snyders[2]

[1]University of Mons, Mons, Belgium [2]University of Mons, ChIPS, Mons, Belgium [3]University of Mons, CMN, Mons, Belgium

damien.thiry@umons.ac.be

Inductively coupled plasma (ICP) discharges are commonly used for plasma polymerization. It is well known that these discharges exhibit two modes of operation as a function of the applied RF power (P_{RF}): capacitive (E mode) at low plasma density and inductive (H mode) at high plasma density. The transition occurs for a critical P_{RF} value ($P_{tr.}$). We recently demonstrated the importance of the E-H transition on the properties of propanethiol plasma polymers (Pr-PPF).
In this work, aiming to gain more understanding on the growth mechanism involved in E and H modes, we have investigated the plasma chemistry by Residual Gas Analysis (RGA) mass spectrometry. These data are correlated with the chemistry of the Pr-PPF films evaluated by X-Ray photoelectron spectroscopy (XPS).
Pr-PPFs were synthesized varying P_{RF} at 20, 40 and 80 mTorr. In E mode ($P_{RF} < P_{tr.}$), the sulfur content is high (%S ~ 40%) and significantly decreases after 20h aging of the films in air. This phenomenon is attributed to the release of sulfur-based molecules (H_2S, CS_2) trapped in the network. In H mode, %S is significantly lower (10 < %S < 25%) and the aging effect is not observed suggesting that, in this case, all sulfur is covalently bonded to the network.
RGA measurements reveal the production of H_2S in both E and H modes. The latter could be trapped during the growth of the film at low P_{RF} but for $P_{RF} > P_{tr.}$, the stronger ionic bombardment and UV photon irradiation could prevent this phenomenon. Moreover, for $P_{RF} > P_{tr.}$, CS_2 is identified illustrating the stronger fragmentation due to the higher electron density in H mode. Based on these data and theoretical calculations using Density Functional Theory, different reactions pathways are proposed.

Keywords
E-H mode transition
propanethiol
sulfur content