Study the effect of the inductive to capacitive transition on propanethiol plasma polymers properties: correlation between film and plasma chemistry

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Inductively coupled plasma (ICP) discharges using a coil as an electrode, which normally exhibit two modes of operation, are commonly used for plasma polymerization.[1-3] At low power, these discharges are characterized by rather low electron density and faint light emission which are common features of the capacitive mode (E). In this case, the discharge is maintained by the electrostatic field developed between the coil extremities. Increasing the power up to a transition value ($P_{tr.}$) results in a shift to the inductive mode (H). In this regime, the plasma is generated by the induced electrical field produced by the oscillating magnetic field as RF current is flowing through the coil. This mode requires sufficiently high electron densities to support the induced currents in the discharge. In H mode, the plasma has about one order of magnitude higher electron density and much stronger light emission. It was shown that these plasma features change abruptly for a power value equal to $P_{tr.}$.[4,5]

The E-H transition was the topic of both theoretical and experimental studies related to Ar, N_2, Ar/ N_2, O_2, Ar/ O_2, H_2 and Ar/H_2 plasmas used mainly for materials etching required e.g. in semiconductor processing, or in biological sterelization.[6,7] Nevertheless, it has received little attention in the plasma polymer field. However, we demonstrated recently the importance of the E-H transition on propanethiol plasma polymers films (Pr-PPF) [8] which could be used as a support for DNA immobilization or gold nanoparticles due to the great affinity between thiol and gold. [9,10] It was shown that the chemical composition of the layers and the chemical stability of the coatings are strongly affected by the mode operation of the coil.

Due to the different chemical properties observed for layers synthesized in E and H mode, one could expect major changes on the plasma chemistry and hence in the growth mechanism involved in each mode. Therefore, in this work, with the aim to gain more understanding on the effect of the E-H transition on the plasma chemistry, mass spectrometry measurements in RGA (“Residual Gas Analysis”) mode were performed.

These data are correlated with the chemical composition of the layers evaluated by *in-situ* and *ex-situ* XPS measurements. The E-H transition as a function of power (P_{RF}) and pressure (p) was observed by using optical emission spectroscopy (OES).[6] The evolution of the deposition rate (R_D) is also monitored using mechanical profilometry since it provides information on the growth mechanism of the layer. Moreover, as a theoretical support to our understanding of the mass spectrometry data, DFT ("Density Functionnal Theory") calculations were performed. Based on this approach, different fragmentation pathways in the plasma have been identified depending on the operation mode of the discharge.

The E-H transition was detected by measuring the mean intensity of the acquired emission spectra. For $P_{RF} = P_{tr.}$, the mean intensity increases markedly and is attributed to the E-H transition (Figure 1 (a)). The $P_{tr.}$value increases as a function of p which is in good agreement with literature data for molecular gas like H_2, O_2 and N_2.[11]Actually, for the discharge to shift from E to H mode, a minimal electron density is required to sustain the induced electrical field. While increasing p, electrons loss more energy through collisional processes including dissociation reactions and rotational/vibrational/electronic excitations. Therefore, a higher power has to be dissipated into the discharge to generate enough ions-electrons pairs allowing the discharge to shift from E to H mode.

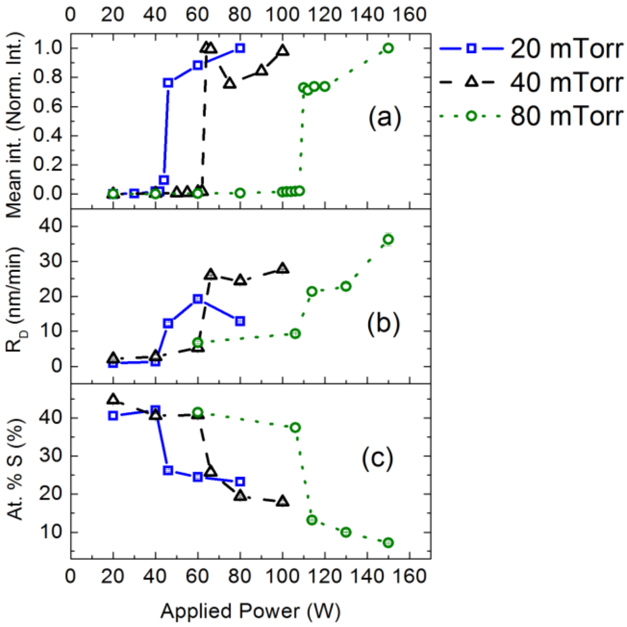

Figure 1 : Evolution of the mean intensity (a), the deposition rate (b) and the atomic sulfur content (c) as a function of the P_{RF} for a p of 20, 40 and 80 mTorr.

Concerning the evolution of R_D for the three p considered in this work, a transition from low to high values appears for $P_{RF} = P_{tr.}$ (Figure 1(b)). That could be explained by the large increase in the concentration of film forming species resulting from the higher number of fragmentations reaction as the electron density in the H mode is higher.

For each p, the evolution of the atomic sulfur content (at.%S) also reveals a strong discontinuity for $P_{RF} = P_{tr.}$ namely a significant lowering (by 40% to 75%) when transiting from the E to the H mode (Figure 1 (c)). This phenomenon could be attributed to the extended fragmentation of the precursor in the H mode which would leads to the loss of S-based fragments by pumping as it is often observed in plasma polymerization.[2]

Moreover, surprisingly, in the E mode, the at.%S is found to be much higher (~40%) than in the precursor (25%). This is quite unusual since most of the time, the plasma polymerization process leads to the loss of functionalities due to fragmentation of the precursor and subsequent pumping of stable molecules.[2] We attribute this observation to the presence, in the plasma polymer network, of unbounded stable molecules presenting a high S/C ratio (e.g H_2S, CS_2). This phenomenon is not observed for films prepared in the H mode probably because, in that case, the energy brought to the film by ions and photons is much higher and lead to the desorption of the trapped sulfur based molecules. Furthermore, the energy of ions and UV photons is high enough to break the organic chemical bonds at the plasma/growing film interface. That could also result in a higher release of the sulfur-containing molecules from the growing film which would additionally decrease the at.%S.

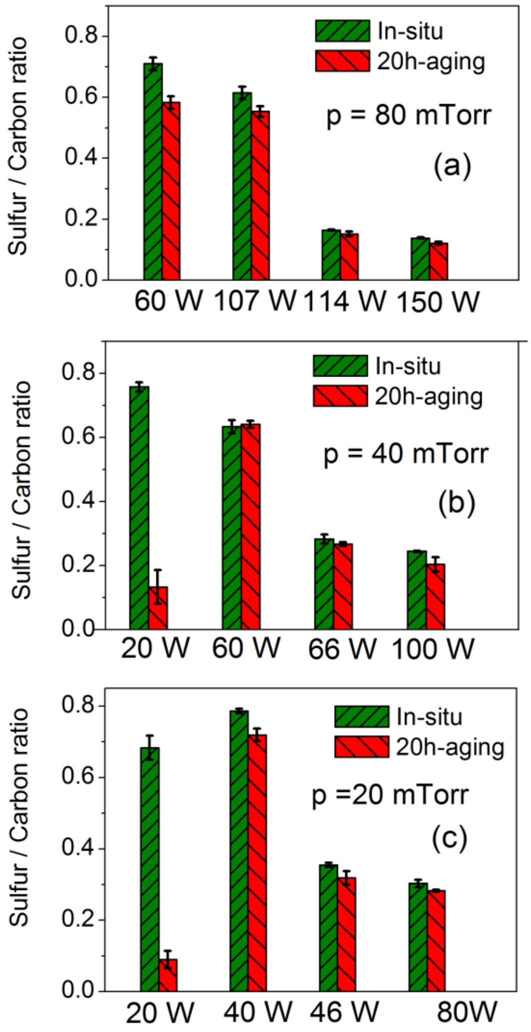

Figure 2 : The evolution of the S/C ratio measured by XPS (i) *in-situ* and (ii) after aging in the air during 20h as a function of P_{RF} for the films synthesized at a p of 80mTorr (a), 40mTorr (b) and 20 mTorr (c).

Based on these observations and in order to study the chemical stability of the coatings, the S/C ratio of E- and H- mode prepared films were measured by XPS after 20h aging in air, and compared with the initial S/C values measured *in-situ*. The data indicate, whatever the p and for the lower P_{RF} used in the E mode, a large decrease of the S/C ratio likely due to the release of the trapped sulfur-molecules in the air supporting our previous explanation. Still in E mode but close to the transition, the behavior is different with the disappearance of the aging effect and as a consequence, a high sulfur content in the films even after aging. This could be explained by the increase of the cross-linking density with P_{RF} at a fixed p as previously reported for allylamine plasma polymers^3. In H mode, whatever the P_{RF}, the Pr-PPF present a lower at.%S which is stable under aging suggesting that in this case, all sulfur atoms are covalently bonded to the film.

Aiming to identify the trapped sulfur molecules and to gain more understanding about the effect of the E-H transition on the plasma chemistry, mass spectrometry measurements in RGA mode were performed (Data not shown). In E mode, H_2S molecules are detected in a large amount in the mass spectra. Being stable, these molecules do not take part to the growth of the film but could be trapped after adsorption explaining the extra sulfur content. Based on DFT calculations, the formation of these molecules is explained trough (i) rearrangement reaction of the precursor induced by electron impact and (ii) an exothermic addition reaction between the precursor and hydrogen atom.

By comparing the mass spectra from E to H mode, the main modifications consist in (i) the complete disappearance of the precursor signal in H mode due to the strong fragmentation and (ii) the important production of CS_2 molecules. In addition to reactions at the growing film interface involving sulfur species, gas phase reactions, supported by DFT calculations were also considered to explain the important presence of these molecules. From theoretical data, it was shown that different reactions pathways leading to the formation of the CS_2

molecules are highly exothermic. At the same time, the concentration of CS_2 in the gas as a function of the process parameters was correlated to the at.%S measured in the synthesized layers. Higher is the CS_2 proportion in the plasma, lower is the at.%S in the films.

The whole set of our data clearly demonstrate that both plasma and film chemistries are strongly influenced by the plasma mode when using an ICP coil. All our findings show that the E-H transition plays a key role defining the growth mechanism of sulfur-based plasma polymers using ICP discharges.

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