Wide Range Control of the Chemical Composition and Optical Properties of Propanethiol Plasma Polymer Films by Regulating the Deposition Temperature

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Abstract

This work reports about the significant impact of the substrate temperature (T_S) on the chemical composition, bond structure, and refractive index of propanethiol plasma polymers. The experiments are conducted for a T_S range (30 ºC to 120 ºC) including the growth temperature that is reached due to the inherent heating observed during plasma polymerization processes. The data highlight the importance of defining T_S in order to reach a real control over the deposition process. Indeed, stabilizing T_S is essential to establish a good correlation between the plasma chemistry and the chemical composition of the films. This allows the identification of some of the plasma species responsible for the high sulfur content reached under certain growth conditions (S > 40%). This knowledge provides an ample control over the sulfur concentration of the films, which enables the refractive index to be tuned within a wide range (1.63 to 1.82).

Introduction

Organosulfur materials are of interest for different technological applications.[1] Among them, the development of new synthetic routes for the deposition of thin films materials with a controllable sulfur (S) concentration is very appealing for the development of high refractive index organic materials ($n > 1.7$).[2] According to the Lorentz-Lorents equation this is accounted by the high molar refraction (i.e. the electrical polarizability)[3] of S based structures typically present in sulfur-containing polymers.[4]

In this context, the plasma polymerization of an organic vapor represents a solvent-free and competitive single-step alternative for the development of functional organic thin films denominated plasma polymer films (PPFs). Such materials find application in different technological fields such as biomaterials,[5] sensing,[6] photonics[7] and as protective barriers.[8] This is so thanks to the inherent advantages of plasma technology, which is already present in different in industrial processes,[9] and of PPFs (good coating adhesion, mechanical and thermal stability, insolubility in organic solvents, and a uniform and pinhole-free surface).[10] However the growth mechanism is complex involving different physicochemical reactions such as the gas phase precursor dissociation, mainly by electron impact, the recombination of the generated species, the surface ion bombardment and UV irradiation, and others. This complexity and the interplay between these phenomena makes it difficult to establish the independent influence of the externally controlled working parameters (working pressure, injected power, substrate bias …) on the final composition of the films. Aiming to contribute to a better understanding of the growth mechanism of PPFs, numerous works have been published during the last years analyzing the chemical reactions occurring in the plasma phase and at the interfaces with the chamber walls (including the substrates) as a function of different working parameters; as well as the influence on the final deposit.[11] Other works deal with the ion bombardment at which the growing films is

exposed during the deposition; and how it affects the retention of target functionalities and the degree of crosslinking of the films.[12] Despite of its importance, in comparision only a few works take into account and investigate the influence of the thermal conditions of the growing film on the surface physicochemical reactions involved during a plasma polymerization process. Some relevant antecedents can be found in the research of Lopez et al. showing a much better retention of the precursor structure when cooling down the substrate holder during the plasma polymerization of both polymerizable and non-polymerizable precursors.[13] Other works have investigated the T_S influence on the deposition rate, composition, and stability of PPFs,[14] confirming the key role of the deposition temperature on the growth mechanism.

Recently, we have investigated the strong impact of the discharge mode (capacitive or inductive coupling) on the atomic surface composition of PPFs grown by the plasma polymerization of propanethiol (PTh).[11a,15] As a general trend, these works reported the deposition of S rich PPFs in the capacitive mode in contrast with the lower S concentration of the films deposited in the inductive mode. The chemical characterization of the species generated in the discharge by mass spectrometry showed the production of moieties with a high S/C ratio (e.g. H_2S) in the capacitive mode.[11a] Nevertheless it was not possible to find a clear correlation between the concentration of some of these species in the discharge and the film composition. Further experiments revealed that in the case of inductively coupled discharges the substrate holder and therefore the growing films, experience a fast heating up to ~ 90 ºC;[16] a phenomenon that affects the composition of the PTh-PPFs. Motivated by these preliminary results, the present work systematically analyzes the independent influence of the plasma chemistry and the thermal conditions of the growing film by externally controlling the T_S during the deposition of PTh-PPFs. Comparison of these studies with our previous

investigations conducted without controlling T_S illustrates the impact of this generally omitted parameter on the incorporation of some of the plasma generated species; this being an issue to be considered in other plasma polymerization processes. Thus, the fine regulation of the deposition temperature enables us to accurately control the chemical composition of the films for fixed plasma conditions. As a practical application, the refractive index of the films is also analyzed illustrating the possibility of the technique to adjust it within a wide range as a function of the S concentration.

Experimental Section

Chemicals and Materials

Propanethiol (PTh) from Sigma Aldrich (99 % purity) was plasma polymerized on 1x1 cm^2 Si wafers washed in methanol.

Deposition Reactor

The depositions were carried out in a radio frequency (RF) plasma reactor described elsewhere[11a] where the plasma discharge is excited by an internal one-turn Cu coil (10 cm in diameter) connected to a RF power supply via a matching network. This type of reactor can be operated in two modes with completely different plasma characteristics.[17] At low plasma power the discahrge is ignited due to the drop of potential between the powered end of the coil and the ground (in this case the reactor walls). This capacitive discharge, also denominated E mode, is characterized by a lower plasma density and weaker optical emission in comparison to the inductively coupled plasma (ICP) or H mode. The latter plasma mode is excited in the same reactor by injecting a RF power higher than a given threshold that depends on the working pressure. Under these conditions the plasma density is high enough to sustain the RF

currents induced in the discharge by the oscillating magnetic field generated by the RF currents circulating through the coil. This leads to the inductive coupling of the power injected into the discharge producing an increase in the plasma density when switching from the E to the H mode. In our experimental set-up and for the used precursor, this behavior was studied by optical emission spectroscopy (OES) in order to determine the threshold power at which the E to H mode transition takes place for the different operation pressures used in this work.[11a] During our experiments the RF power (P_{RF}) and the working pressure (P) were varied in the range 20 W to 150 W and 20 mTorr to 80 mTorr, respectively. Most of experiments presented here were carried out at a fixed pressure of 40 mTorr for which an abrupt transition from the E to the H mode was observed at ~ 60 W.[11a] In all the experiments the substrate holder was located at 10 cm from the coil and the precursor flow was fixed to 10 sccm. The system permits to accurately control T_S by combining a liquid nitrogen cooling system with an ohmic heating circuit.

Characterization Techniques

X-ray Photoemision Spectroscopy (XPS) analyses were performed using a PHI 5000 VersaProbe apparatus connected under vacuum to the deposition chamber. A monochromatized Al K_α line (1486.6 eV) was used. More details can be found elsewhere.[11a] Depth profile analyses were carried out by sputtering the samples with a C_{60}^+ ion source operated at 10 nA and 10 kV with a raster area of 2x2 mm^2 at an incident angle of 70°. Such a kind of polyatomic sputtering source is particularly suitable for the characterization of soft materials such as organic films since it significantly reduces the damage caused by the impinging ions in the "bulk" of the sample, in comparison to conventional monoatomic sources. This methodology has

been successfully tested for the depth profile analyses of polymers.[18] The sputtered thickness (i.e. the analysis depth) was calculated by multiplying the sputtering time by the sputtering rate; which in turn was roughly estimated by dividing the film thickness by the sputtering time at which the C 1s and S 2p signals start to deplete and the native SiO_2 layer of the Si substrate is detected.

The films were also investigated by Fourier Transform Infrared Spectroscopy (FT-IR) using an Excalibur FTS 3000 FT-IR spectrometer from Bio-RAD. Spectra from 400 cm^{-1} to 4000 cm^{-1} were recorded with a resolution of 4 cm^{-1} and averaged over 2048 scans in order to accumulate a good signal-to-noise ratio.

In order to determine the deposition rate (R), the thickness of the layers was measured using a Sloan Dektak 3030ST mechanical profilometer.

The refractive index of the films was calculated by a variable angle spectroscopic ellipsometer W-VASE M2000X from J.A.Woollam., Inc. Ellipsometric data were analyzed by combining the Cauchy dispersion law and B-Spline relations using a CompleteEase software.

The plasma composition was investigated by a quadrupole HAL EQP 1000 mass spectrometer from Hiden Analytical operated in the residual gas analysis (RGA) mode and connected to the chamber by a 100 μm extraction orifice. In order to detect neutral species, they were ionized by low energy electron impact of 20 eV intending to prevent excessive fragmentation of the precursor in the ionization chamber. Nevertheless raw mass spectrometry data were treated, as it is described in a previous work,[16a] in order to correct the spurious contribution of the species generated by fragmentation of the precursor in the spectrometer.

Results and Discussion

Depositions at Fixed Substrate Temperature (T_S = 30 ºC)

In order to assess the influence of the plasma mode on the sample composition independently of the sample heating; a first set of experiments analyzes a group of samples grown by stabilizing T_S. For sake of comparision some experiments conducted whithout controlling Ts are included in this study.

Figure 1a shows the sulfur concentration as a function of the plasma power for a set of samples deposited at T_S = 30 ºC and without controlling T_S at P = 40 mTorr. In both sets of experiments, two groups of samples can be distinguished depending on the applied power: (i) films grown at $P_{RF} \leq 60$ W and (ii) those deposited at higher powers. This result is understood by considering the abrupt transition from the E to the H mode that our PTh discharge experiences at $P_{RF} \sim 60$ W at this pressure.[11a] The PPFs deposited in the E mode ($P_{RF} \leq 60$ W) are characterized by a very high sulfur concentration (S > 40 %) that contrasts with the lower S content of the H-mode samples (P_{RF} > 60 W). The most remarkable trend in the figure is how, for all the inspected powers, the PPFs deposited at T_S = 30 ºC present a higher S content than those grown without controlling this parameter. This is particularly noticeable in the case of the more energetic H-mode discharges. For instance, at P_{RF} = 100 W note the low S content of the sample deposited without controlling T_S (S = 18 %) in comparison to the rather high concentration obtained at T_S = 30 ºC (S = 36 %), which is higher than the S content of the starting precursor (S = 25 %). Such a behavior is related to the intrinsic heating of the sample during the deposition process, which is more intense for the H-mode discharges (e.g. $T_S \sim 90$ ºC after 30 min at P_{RF} = 100 W).[16a] This confirms the important influence of the thermal conditions of the growing film on the composition of the ICP deposited PTh-PPFs, even for plasma powers lower than what were reported before. Thus stabilizing the substrate temperature is an effective way for the H-mode

deposition of PTh-PPF with a high S content (higher than in the starting precursor),
even for the most energetic discharge, e.g. S = 36 % at P_{RF} = 100 W. Although the latter
value is not as high as the 40 % of sulfur for the E-mode samples; it is worth
mentioning here the high deposition rate of the sample deposited at P_{RF} = 100 W (R =
70 nm · min^{-1}) in contrast with the E-mode samples (e.g. R = 5 nm · min^{-1} for P_{RF} = 60
W), a particularly important issue for the potential industrial transfer of these results for
the development of S rich materials.
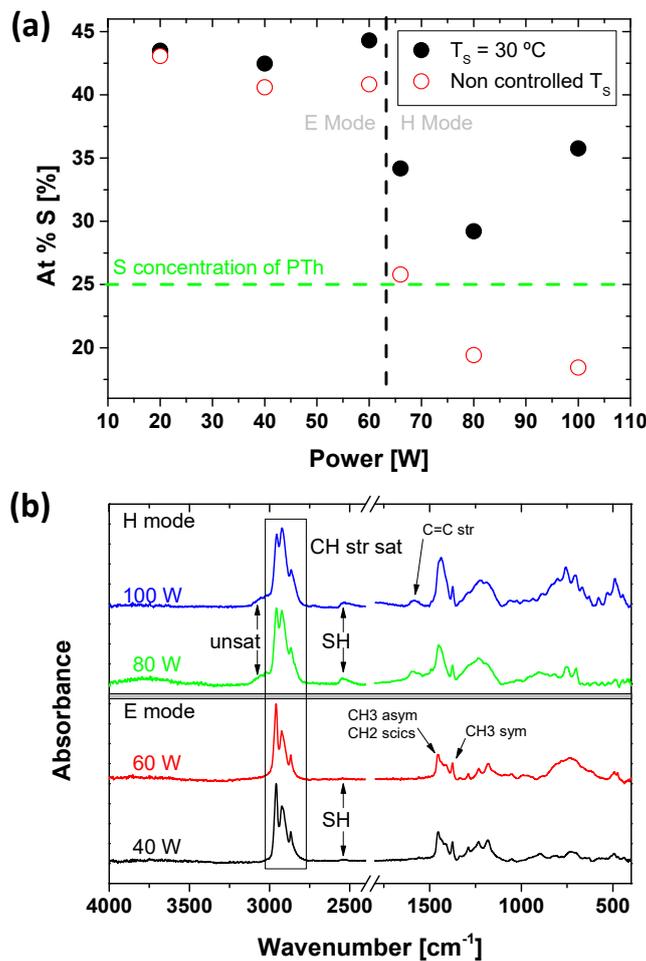
Figure 1. (a) Atomic concentration of sulfur (in-situ XPS analyses) as a function of the
deposition power for a set of samples (P = 40 mTorr) deposited at T_S = 30 ºC (black
filled) and at not controlled T_S (red empty). The dashed black line indicates the E to H
mode transition and the dashed green line the sulfur concentration of the starting
precursor (PTh) not considering hydrogen atoms. (b) FT-IR spectra of the same samples
deposited at T_S = 30 ºC.

Besides the chemical composition, the plasma regime also and the injected power affect the bulk chemical structures of the films (see FT-IR spectra in Figure 1b). Attribution of the IR bands has been done according to the literature.[19] Comparison of the E- and H-mode IR spectra shows some changes in the bond structure of the films. The most evident trend is the modification in the relative intensities of the CH stretching modes in saturated structures (vibration bands at 2960 cm^{-1} and 2925 cm^{-1}) indicating an increase in the concentration of methylene groups in comparison to the methyl terminations as P_{RF} increases. This agrees with the evolution of the relative intensities of the features at 1455 cm^{-1} (CH$_3$ and CH$_2$ deformations) and at 1380 cm^{-1} (only due to CH$_3$ deformations). Such a behavior may indicate an increase of the length of the structures forming the PPF matrix, and a less branched and likely more cross-linked polymeric structure. Moreover, it is possible to recognize the development of the CH stretching modes of unsaturated groups at $v > 3000$ cm^{-1}, as well as the development of the C=C stretching of conjugated structures at 1590 cm^{-1} in the H-mode samples. The formation of unsaturated groups may also account for the reduction of methyl groups. Both set of samples present a very weak signal at 2540 cm^{-1} corresponding to the thiol stretching. Regarding this latter vibration it is worth noting its very low IR-absorption cross-section that justifies the low intensity in the spectra. In the range between 1500 cm^{-1} and 1000 cm^{-1} E-mode samples present rather well defined features that are atributed as follows: the medium-intensity broad band at 1455 cm^{-1} to CH$_3$ asymmetric and CH$_2$ scissor deformation modes; the shoulder at 1420 cm^{-1} to CH$_x$ deformation modes whose frequency is raised by the presence of S atoms; the CH$_3$ symmetric deformation at 1380 cm^{-1}; the weak band at 1340 cm^{-1} attributed to C-H deformation in saturated cross-linked structures; the band at 1290 cm^{-1} to out of plane modes of saturated methylene groups in the presence of sulfur atoms, and features at 1180 cm^{-1}

and 1050 cm^{-1} both related to C-C and/or C-S vibrations and the CH$_3$ rocking. In this region the H-mode samples present broader features, an effect that is attributed to a higher heterogeneity of the chemical groups responsible for vibrations in this region, as well as to a higher degree of crosslinking as reported for other plasma polymerization processes.[20] Most of these trends are related to the higher plasma density of the H discharges which leads to a higher precursor fragmentation and degree of crosslinking, as well as to the formations of new structures (e.g. unsaturated groups).

The high sulfur concentration of the PTh-PPFs was tentatively related to the generation of S based species presenting a high S/C ratio, as revealed by our theoretical simulations and RGA mass spectrometry analyses.[11a] In order to establish a correlation between the plasma phase and the film composition, as well as intending to identify the plasma species responsible for the high sulfur content of the films; new experiments extended the experimental window to other pressure and plasma power ranges (**Table 1**). The experimental conditions were selected in order analyze the plasma chemistry when exciting E-mode and H-mode plasmas at three different pressures. A detail description of the mass spectra acquired under these plasma conditions during the plasma polymerization of PTh in our ICP reactor can be found elsewere.[11a] In general these analyses reveal the production of different carbon-based ($[C_yH_x]^+$), hydrogenated sulfur ($[H_xS]^+$) and carbon/sulfur-based species ($[C_yH_xS]^+$) according to a complex fragmentation pattern that was theoretically simulated in a previous work.[11a] These mass spectrometry analyses shown the production of different species with a high S/C ratio; particularly H$_2$S which corresponds to the most intense peak in the E-mode spectra. Thus the incorporation of H$_2$S together with other S rich species was tentatively proposed to account for the high S content in some PTh-PPFs. In order to confirm this hypothesis **Figure 2** plots the S content vs. the relative concentration of H$_2$S molecules

in the glow discharge ($I_{rel.}(H_2S)$), which is calculated by using **Equation (1)** from the mass spectrometry data previously reported.[11a]

$$I_{rel.}(H_2S) = \frac{I_C(H_2S)}{I_C(m/z=15) + \sum_{m/z=26}^{m/z=29} I_C(m/z) + \sum_{m/z=39}^{m/z=43} I_C(m/z)} \qquad (1)$$

In this equation $I_{rel.}(H_2S)$ is calculated as the ratio between the corrected intensity (see experimental section) of the H_2S peak (m/z = 34) and the sum of the corrected intensities of those peaks identified with film forming carbon containing species. The $I_{rel.}(H_2S)$ values calculated for the different plasma conditions are reported in **Table 1**. In a first attempt these experiments were carried out without controlling T_S during the deposition (Figure 2a). Although, at first sight, a gradual increase of the S concentration with the production of H_2S in the discharge is observed; there is an important disagreement between the H- and E-deposited films. This is highlighted in Figure 2a with blue arrows. This discrepancy might be related to the fast heating that the substrate holder, and therefore the growing films, experience during the H-mode depositions. Therefore new experiments were repeated fixing T_S at 30 ºC (Figure 2b). While stabilizing T_S, a linear relationship between the H_2S density in the glow discharge and the S content in the PPFs was found. This is an important result that allows the identification of H_2S as one of the species contributing to the sulfur content of the films. Therefore at fixed and low deposition temperature (T_S = 30 ºC) the composition of the films is regulated by gas phase chemial reactions leading to a high production of sulfur rich species (e.g. H_2S) in the discharge. Nevertheless, extrapolation of the linear fit in Figure 2b to a zero production of H_2S still allows a sulfur content of 19 % indicating the influence of other S based species. As a final remark, comparison of Figure 2 (a) and (b)

illustrates the critical influence of T_S on the PPF chemistry and therefore likely on the PPF properties. Indeed the absence of linear behavior in those experiments executed without controlling T_S (Figure 2a) highlights the need for controlling this parameter to suitably understand plasma polymerization processes.
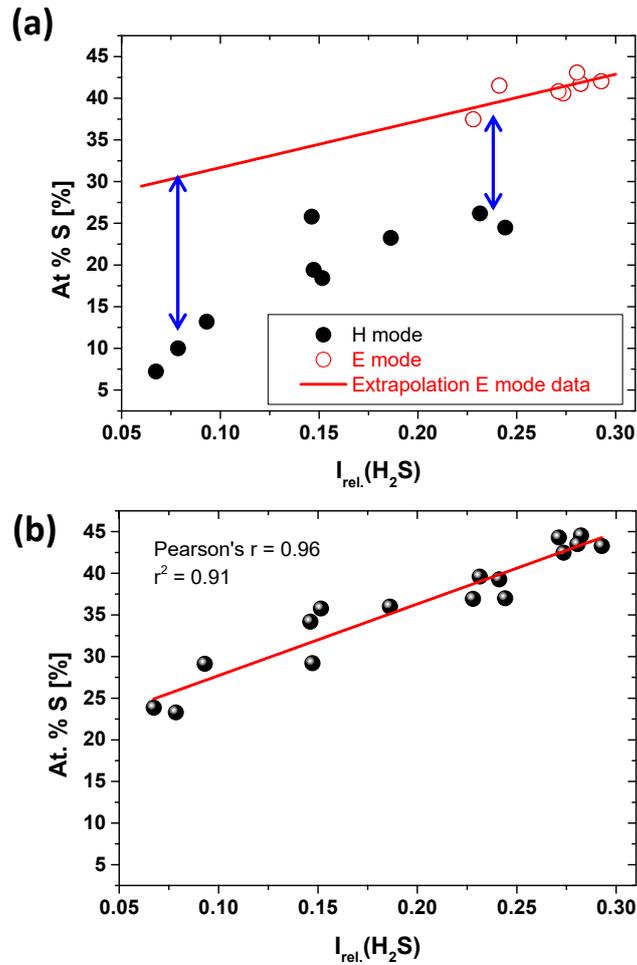
Figure 2. Atomic concentration of sulfur vs. the relative abundance of H_2S in the discharge ($I_{rel.}(H_2S)$) for: (a) PTh plasma polymers deposited without controlling T_S, and (b) when fixing T_S at 30 ºC.

Table 1. Plasma parameters and $I_{rel.}(H_2S)$ values of the discharges analyzed in Figure 2.

Pressure [mTorr]	Power [W]	$I_{rel.}(H_2S)$	Discharge mode
20	20	0.28	E mode
20	40	0.29	E mode
20	46	0.23	E-H transition
20	60	0.24	H mode
20	80	0.19	H mode
40	20	0.28	E mode
40	40	0.27	E mode
40	60	0.27	E mode
40	66	0.15	E-H transition
40	80	0.15	H mode
40	100	0.15	H mode
80	60	0.24	E mode
80	107	0.23	E mode
80	114	0.09	E-H transition
80	130	0.08	H mode
80	150	0.07	H mode

Substrate Temperature Study

A new set of experiments were carried out by fixing the plasma conditions (40 mTorr and 100 W, H-mode discharge) in order to analyze the influence of T_S. **Figure 3**a shows the semilog plot of the deposition rate as a function of the reciprocal substrate temperature. These data in the figure can be linearly fitted according to an Arrhenius law. Within the studied range of temperatures (30 ºC to 120 ºC), the deposition rate decreases with T_S and a negative apparent activation energy (E_a) for the film growth process of -26 kJ · mol^{-1} is calculated. A possible model that accounts for this behavior was propoused by D'Agostinto and coworkers.[14a,b] This takes into account the

influence of T_S on the surface adsorption/desorption processes and polymerization reactions involved in the film growht. Assuming the Langmuir formulation for the surface coverage degree the following **Equation (2)** is obtained for the deposition rate, where: k_r is the reaction rate of the surface polymerization reaction, n_{ss} is the number density of surface sites activated for the polymerization raction, $K = k_a/k_d$ is the adsorption/desoption equilibrium constant, and $[R_g]$ is the concentration of film forming species in the plasma phase.

$$R = n_{ss}k_r\frac{K[R_g]}{1+K[R_g]} \quad (2) \; ; \qquad R \approx n_{ss}k_rK[R_g] \quad (3) \; ; \qquad R \approx n_{ss}[R_g]e^{-\frac{E_r+\Delta H_{ads}}{RT_S}} \quad (4)$$

Considering the low deposition pressure and wheigt of the plasma generated species, for the range of temperatures explored here it is reasonable to assume that desorption largely exceeds adsorption ($K[R_g]\ll1$) and therefore Equcation (2) can be aproximated to **Equation (3)**. In this eqution both k_r and K follows an Arrhenius law (**Equation (4)**) where $E_r > 0$ is the activation energy of the surface polymerization reaction and $\Delta H_{ads} < 0$ is the heat of adsorption of the film forming species. Therefore the apparent activation energy of the deposition process is $E_a = E_r + \Delta H_{ad}$; and the negative value of E_a indicates that for these energetic plasma conditions (i.e. H-mode discharge, $P_{RF} = 100$ W) the kinetics of the growth mechanism is mainly controlled by the adsorption/desorption processes.[14a,21]
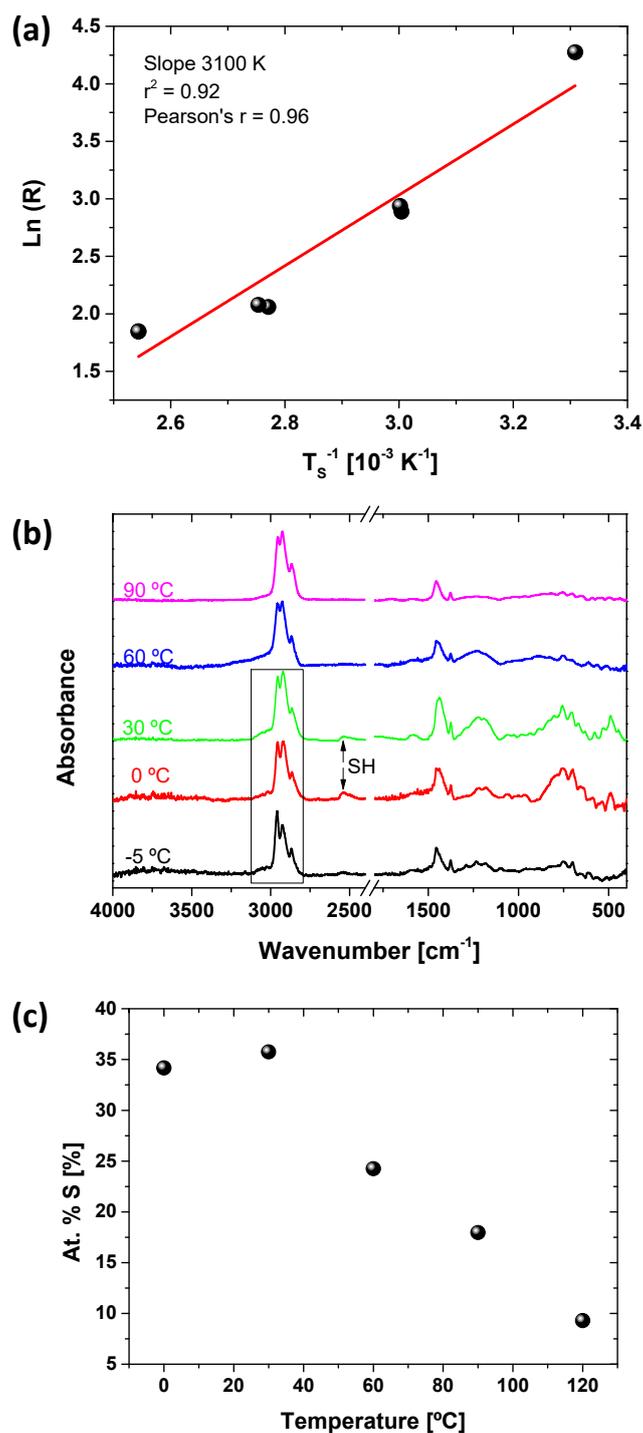
Figure 3. Deposition rate and composition of PTh-PPFs deposited at 40 mTorr and 100 W. (a) Arrhenius plot of the deposition rate vs. T_S^{-1}. (b) FT-IR spectra and (c) Atomic concentration of sulfur as a function of T_S (in-situ XPS).

FT-IR spectra of a representative set of samples deposited at fix H-mode plasma conditions (P = 40 mTorr and P_{RF}= 100 W) are presented in Figure 3b. The figure shows the loss of the thiol signal when heating the substrate at $T_S > \sim 40$ ºC. This

finding points out the likely key role played by T_S for the synthesis of PPFs with target functionalities, e.g. the thiol function proposed to enhance the adhesion of gold nanoparticles.[1c] As T_S increases, it is also obvious the broadening and intensity decrease of some IR features, mainly those at $v < 1500$ cm^{-1}. It is also important to stress how when cooling the substrate holder down to temperatures lower than 0 ºC, the IR spectrum depicts a profile similar to those observed in the E-mode samples (c.f. Figure 1a, particularly the relative intensities of the CH$_3$ and CH$_2$ asymmetric stretching bands). All these trends indicate a higher degree of crosslinking and a lower retention of precursor functionalities as T_S increases. This behavior can be rationalized by considering the energy density dissipated during the growth of the film by ion bombardment (ε_{surf});[12c,d] which is given by **Equation (5)** where Γ_i and $<E>$ are the ion flux impinging over the growing film and the mean ion energy, repectively.

$$\varepsilon_{surf} = \frac{\Gamma_i <E>}{R} \qquad (5)$$

Therefore, decreasing the deposition rate (i.e. substrate heating, cf. Figure 3a), increases the energy density of the ion bombardement, which leads to a higher crosslinking degree and a lower retention of the precursor structure.[12d] In this regards, it has been recently reported how the degree of crosslinking and the precursor fragmentation can be accurately controlled as a function of the deposition rate (in our case controlled by T_S for a fixed plasma conditions), this being an effective strategy to regulate the preservation of the precursor integrity in remote plasma polymerized thin films.[20]

Regarding the surface composition, in-situ XPS data (Figure 3c) shows how the S concentration gradually decreases with T_S in the 30-120 ºC range. This agrees with the depletion of the thiol vibration in Figure 3b. Such effects could be partially accounted by the increase of the energy density delivered on the surface by ion bombarding (c.f. Equation 5 and the influence of T_S on R in Figure 3a). However this was reported to

have a rather low impact on the atomic composition of PPFs.[12c,20] Therefore the evolution of the S sulfur content is also tentatively related to a dissimilar influence of T_S over the adsorption/desorption kinetics of the plasma generated species on the growing films. Sulfur rich stable species (e.g. H_2S) generated in the plasma discharge may be physically absorbed on the growing film. As indicated above, for these deposition conditions the thermodinamic adsorption/desorptium equilibrium is shifted towards desorption; and the adsorbates can either diffuse until finding a reactive site where they become irreversibly chemisorbed, or return to the gas phase via thermal desorption. In this regards, the Frenkel equation states that the residence time of the adsorbates before desorption exponentially increases with T_S^{-1}.[22] Therefore, the evolution observed in Figure 3c most probably indicates that the surface residence time of the species with a high S/C ratio is more affected by the thermal conditions of the growing film. Thus, decreasing T_S would prolong their residence time on the nascent film and therefore increases the probability of incorporation, either by chemisorption on the reactive plasma polymer surface or via physical entrapping into the growing film.

Aging, Bulk Composition and Optical Properties

As illustrated in Figure 2 and 3b, decreasing T_S is an effective way to increase the S concentration of the H-mode deposited PTh films (e.g. in Figure 3c). Although the samples deposited in the E mode ($P_{RF} \leq 60$ W in Figure 1a) present a higher S concentration, our previous studies showed an important loss of sulfur for some of the E-mode samples after one day of aging, particularly in the cases of those deposited at lower power.[15] This issue can be overcome by increasing P_{RF} up to the edge of the E-H transition. However this is a complicated task that involves high efforts to stabilize the E-mode discharge at the edge of the transition threshold, as well as a previous fine

characterization of the discharge in order to determine the transition power. Motivated by these results and their high sulfur content, the stability of the H-mode samples grown at 30 ºC was also analyzed. **Figure 4**a shows the evolution of the surface composition determined by XPS (note that all these measurements except the first one were carried out ex-situ) of a representative example of H-mode sample grown at 30 ºC. This graph clearly shows how the S percentage just slightly decreases after one day of aging, in a similar way to what was observed for those H-mode samples deposited without controlling T_S and therefore with a much lower S concentration. In this regard it is important to remark the much higher stability of the samples analyzed in Figure 4a in comparison to the low-power E-mode samples.[15] During a prolonged aging this process gradually and slowly continues until reaching a stable value of ca. 27 %, which is still a high concentration similar to the S content of the PTh molecule. Parallel to this evolution it is also possible to recognize the oxidation of the surface. This latter result, as well as the loss of surface heteroatoms or more specific chemical functionalities is a usual behavior in plasma polymers that can be related to both surface reactions and diffusional processes.[23] In order to assess the bulk atomic composition of the films, a chemical depth-profile was obtained using a C_{60}^{+} ion gun. Figure 4b shows the overall depth profile of an H-mode PTh-PPF ($P = 40$ mTorr and $P_{RF} = 100$ W) deposited at 30 ºC after 4 months of aging. In this figure clearly observed how the aging process just affects the film surface. Indeed, after sputtering the topmost layer the bulk composition remains stable along the whole sample thickness with a composition similar to what was observed in the surface of the freshly prepared sample (XPS in-situ analysis in Figure 3c). This indicates that the loss of sulfur is due to surface reactions that do not affect the bulk compostion. The homogenous depth profile of this sample contrasts with the

gradient composition observed in the H-mode samples deposited without controlling T_S,[16b] which is accounted by the gradual sample heating during the depostion process.
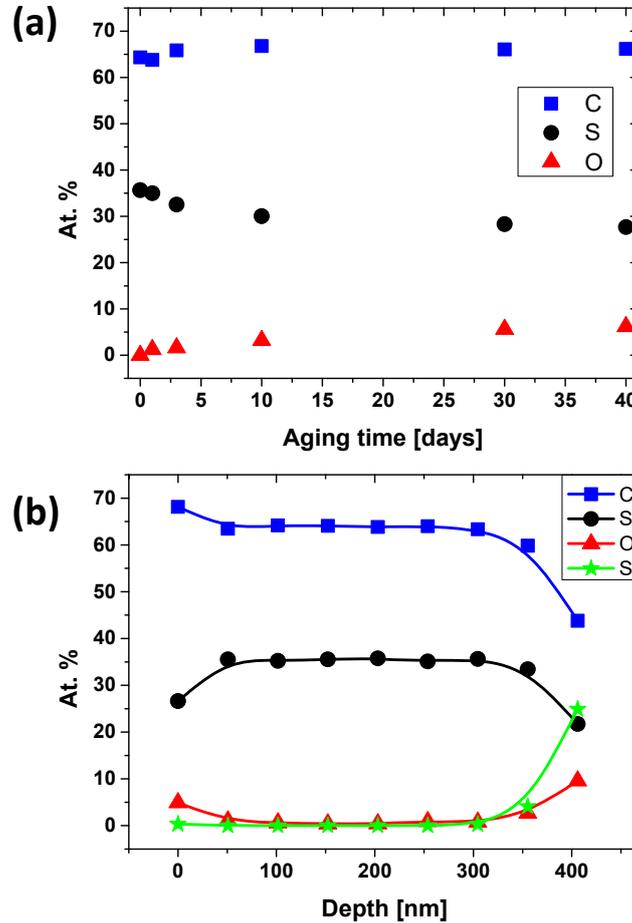
Figure 4. (a) Evolution of the sulfur concentration of an H-mode plasma polymer (P = 40 mTorr and P_{RF} = 100 W) deposited at 30 ºC. (b) Depth profile of the same sample after 4 months of aging.

Finally, and as a potential application, the optical properties of the PTh-PPFs were also analyzed. As indicated in the introduction, organosulfur moieties present a high molar refraction.[4] Hence the sulfur concent has been reported to regulate the refractive index of organic materials.[24] In the case of the PTh discharges, the S concentration can be easily regulated (10 % to 40 %) by combining both: the control that the discharge mode provides over the plasma chemical composition[11a] and the high impact of T_S on the incorporation of S based species. As illustrated by **Figure 5**, this enables the

refractive index of the PTh-PPFs to be regulated within a wide range (1.63 to 1.82 at 589 nm). In this regard, it is important to stress that the latter value is one of the highest refractive index reported not only in case of plasma polymers but also when comparing conventional optical polymers.[4] Moreover the correlation between the refractive index and the film composition presented in Figure 5 allows the development of graded refractive index materials.[25]
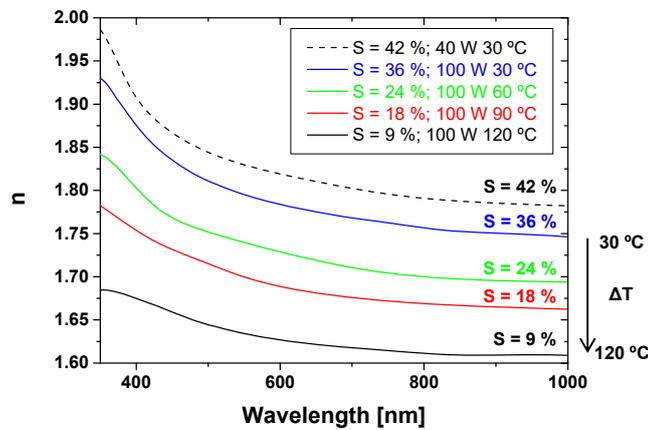
Figure 5. Refractive index curves of PPFs with different S concentration.

Conclusions

The set of results presented here proves the critical influence of the substrate temperature on the chemical composition and characteristics of PTh plasma polymers synthetized in an ICP plasma reactor. According to this information, some of our previous experiments on this system have been revised by controlling this parameter. This alows us to establish the influence of the discharge mode (controlled by the plasma power) on the films characteristics independently of the spurious heating observed previously. This independent control enables correlating the film composition with the plasma chemistry (RGA mass spectrometry) of E-mode and H-mode discharges excited at different pressures. From these analyses, we have identified H_2S as one of the plasma

generated species having the highest impact on the chemical composition of the samples. Moreover, T_S has been revealed to be another critical factor that regulates the chemical composition and structure of the films. In view of the two sets of experiments performed (fixed T_S and variable P_{RF}; and fixed plama considionts and variable T_S) the chemical composition of the films is affected by both: plasma phase processes leading to the production H_2S and other sulfur rich species in the discarge; and T_S which modulates the incorporation of these species into the growing film. Substrate temperature effects are tentatively explained by the thermally controlled equilibrium between adsorption/desorption processes during the deposition and its influence on: the deposition rate, the energy density delivered by ion bombardement, and on the surface residence time of sulfur-rich plasma generated species. Our results show that the simultaneous control of the plasma chemisty (regulated by P_{RF} and the working pressure) and T_S (controling the surface reactions) enables the synthesis of stable and homogeneous PTh-PPFs with a high sulfur concentration. From a practical point of view, this general understanding of the main parameters controlling the S content of the films is used for the synthesis of plasma polymer film with a tailored refractive index. Particularly, PPFs with a high refractive index have been developed, a material with potential as optical coatings.

It is important to that the experiments presented correspond to substrate temperatures of 30 ºC to 120 ºC. Such a temperature range falls within the inherent heating observed during plasma polymerization and other deposition processes. Thus, taking into account the high vapor pressure of some commonly used plasma-polymer precursors, the results and arguments reported here illustrate the need of monitoring this parameter during plasma polymerization deposition processes.

References

[1]   a) Y. NuLi, Z. Guo, H. Liu, J. Yang, *Electrochem. Commun.* **2007**, *9*, 1913; b) A. Marrocchi, D. Lanari, A. Facchetti, L. Vaccaro, *Energy Environ. Sci.* **2012**, *5*, 8457; c) V. Švorčík, A. Chaloupka, K. Záruba, V. Král, O. Bláhová, A. Macková, V. Hnatowicz, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2009**, *267*, 2484; d) M. S. Silverstein, I. Visoly-Fisher, *Polymer* **2002**, *43*, 11.

[2]   S. D. Bhagat, J. Chatterjee, B. Chen, A. E. Stiegman, *Macromolecules* **2012**, *45*, 1174.

[3]   C. W. Bunn, R. d. P. Daubeny, *Transactions of the Faraday Society* **1954**, *50*, 1173.

[4]   J.-G. Liu, M. Ueda, *J. Mater. Chem.* **2009**, *19*, 8907.

[5]   M. C. Vasudev, K. D. Anderson, T. J. Bunning, V. V. Tsukruk, R. R. Naik, *ACS Applied Materials & Interfaces* **2013**, *5*, 3983.

[6]   I. Blaszczyk-Lezak, F. J. Aparicio, A. Borrás, A. Barranco, A. Álvarez-Herrero, M. Fernández-Rodríguez, A. R. González-Elipe, *J. Phys. Chem. C* **2009**, *113*, 431.

[7]   F. J. Aparicio, M. Holgado, A. Borras, I. Blaszczyk-Lezak, A. Griol, C. A. Barrios, R. Casquel, F. J. Sanza, H. Sohlström, M. Antelius, A. R. González-Elipe, A. Barranco, *Adv. Mater.* **2011**, *23*, 761.

[8]   R. Morent, N. De Geyter, T. Jacobs, S. Van Vlierberghe, P. Dubruel, C. Leys, E. Schacht, *Plasma Process. Polym.* **2009**, *6*, S537.

[9]   R. d'Agostino, P. Favia, C. Oehr, M. R. Wertheimer, *Plasma Process. Polym.* **2005**, *2*, 7.

[10]   F. J. Aparicio, I. Blaszczyk-Lezak, J. R. Sánchez-Valencia, M. Alcaire, J. C. González, C. Serra, A. R. González-Elipe, A. Barranco, *J. Phys. Chem. C* **2012**, *116*, 8731.

[11]   a) D. Thiry, N. Britun, S. Konstantinidis, J.-P. Dauchot, M. Guillaume, J. Cornil, R. Snyders, *J. Phys. Chem. C* **2013**, *117*, 9843; b) J. Friedrich, *Plasma Process. Polym.* **2011**, *8*, 783; c) D. Thiry, R. Francq, D. Cossement, M. Guillaume, J. Cornil, R. Snyders, *Plasma Process. Polym.* **2014**, *11*, 606; d) S. Ligot, M. Guillaume, P. Raynaud, D. Thiry, V. Lemaur, T. Silva, N. Britun, J. Cornil, P. Dubois, R. Snyders, *Plasma Process. Polym.* **2015**, *12*, 405.

[12]   a) D. Mansuroglu, S. Manolache, *Plasma Process. Polym.* **2015**, *12*, 1036; b) D. Hegemann, U. Schütz, E. Körner, *Plasma Process. Polym.* **2011**, *8*, 689; c) H. Dirk, *J. Phys. D: Appl. Phys.* **2013**, *46*, 205204; d) D. Hegemann, E. Körner, N. Blanchard, M. Drabik, S. Guimond, *Appl. Phys. Lett.* **2012**, *101*, 211603.

[13]   a) G. P. López, A. Chilkoti, D. Briggs, B. D. Ratner, *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2427; b) G. P. Lopez, B. D. Ratner, *Langmuir* **1991**, *7*, 766.

[14]   a) R. D'Agostino, F. Cramarossa, F. Fracassi, E. Desimoni, L. Sabbatini, P. G. Zambonin, G. Caporiccio, *Thin Solid Films* **1986**, *143*, 163; b) P. Favia, R. Lamendola, R. d'Agostino, *Plasma Sources Sci. Technol.* **1992**, *1*, 59; c) H. Yasuda, *Luminous Chemical Vapor Deposition and Interface Engineering*, Marcel Dekker, New York, USA **2004**; d) H. Yasuda, C. R. Wang, *Journal of Polymer Science: Polymer Chemistry Edition* **1985**, *23*, 87; e) T. B. Casserly, K. K. Gleason, *Chem. Vap. Deposition* **2006**, *12*, 59.

[15]   D. Thiry, N. Britun, S. Konstantinidis, J.-P. Dauchot, L. Denis, R. Snyders, *Appl. Phys. Lett.* **2012**, *100*, 071604.

[16]   a) D. Thiry, F. J. Aparicio, N. Britun, R. Snyders, *Surf. Coat. Technol.* **2014**, *241*, 2; b) D. Thiry, F. J. Aparicio, P. Laha, H. Terryn, R. Snyders, *J. Vac. Sci. Technol., A* **2014**, *32*, 050602.

[17]   P. Chabert, N. Braithwaite, *Physics of Radio-Frequency Plasmas*, Cambridge University Press, Cambridge, UK **2011**.

[18]   a) T. Nobuta, T. Ogawa, *J. Mater. Sci.* **2009**, *44*, 1800; b) K. Tanaka, N. Sanada, M. Hikita, T. Nakamura, T. Kajiyama, A. Takahara, *Appl. Surf. Sci.* **2008**, *254*, 5435.

[19]   a) G. Sokrates, *Infrared Characteristic Group Frequencies: Tables and Charts*, Wiley-Interscience, New York, USA **1994**; b) S. Higuchi, E. Kuno, S. Tanaka, H. Kamada, *Spectrochimica Acta Part A: Molecular Spectroscopy* **1972**, *28*, 1335.

[20]   F. J. Aparicio, M. Alcaire, A. Borras, J. C. Gonzalez, F. Lopez-Arbeloa, I. Blaszczyk-Lezak, A. R. Gonzalez-Elipe, A. Barranco, *J. Mater. Chem. C* **2014**, *2*, 6561.

[21]   a) A. M. Wrobel, I. Blaszczyk-Lezak, P. Uznanski, B. Glebocki, *Plasma Process. Polym.* **2011**, *8*, 542; b) H. Kersten, H. Deutsch, H. Steffen, G. M. W. Kroesen, R. Hippler, *Vacuum* **2001**, *63*, 385.

[22]   A. v. Keudell, *Plasma Sources Sci. Technol.* **2000**, *9*, 455.

[23]   a) H. Jiang, J. T. Grant, J. Enlow, W. Su, T. J. Bunning, *J. Mater. Chem.* **2009**, *19*, 2234; b) K. S. Siow, L. Britcher, S. Kumar, H. J. Griesser, *Plasma Process. Polym.* **2006**, *3*, 392.

[24]   J. W. Chan, H. Zhou, C. E. Hoyle, A. B. Lowe, *Chem. Mater.* **2009**, *21*, 1579.

[25]   L. Martinu, D. Poitras, *J. Vac. Sci. Technol., A* **2000**, *18*, 2619.

The table of contents entry.

Sulfur-rich, stable, and depth-homogenous plasma polymer films are grown by counteracting the spontaneous heating during the plasma polymerization of propanethiol in an inductively coupled plasma. Low-temperature substrate heating is revealed to be an effective strategy to regulate the sulfur content in the sample. This, in turn, is used to tailor the refractive index of the film over a wide range.

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Title: Wide Range Control of the Chemical Composition and Optical Properties of Propanethiol Plasma Polymer Films by Regulating the Deposition Temperature

ToC figure and graphical abstract