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Effect of the substrate temperature on the chemical composition of propanethiol plasma polymer films

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Abstract: In this work, aiming to gain new insights on the layer growth mechanism of propanethiol plasma polymers, the influence of the substrate temperature on the chemical composition of the coatings was investigated. The examination of the data reveals a strong dependence between the sulfur content and the substrate temperature through the presence of trapped sulfur-based molecules in the plasma polymer network. This works paves the way for a better control of the layer properties.

Keywords: Plasma Polymer, Propanethiol, Substrate Temperature, Sulfur Content

During last decades, deposition of organic films by plasma polymerization has become a well-established technique for the synthesis of functional thin films with application in different fields such as photonics [1], biomaterials [2] and protective coatings [3].

We have recently investigated the plasma polymer growth from propanethiol discharge [4, 5]. These works have demonstrated that the atomic sulfur content in the layers can be adjusted within a large range (from 17% to 40%). Such a high sulfur concentration is of interest for the development of high refractive index plasma polymer for optical applications [6, 7]. With the help of DFT calculations and mass spectra analysis, those studies revealed the influence of the plasma chemistry on both the film composition and stability against aging [5]. Particularly it was proposed the physical trapping of the H_2S molecules to account for the high sulfur concentration observed in these films. However, some aspects about the impact on the energetic conditions at the surface (particularly on the substrate temperature) and their influence on the films properties remain unclear.

Although often omitted for the interpretation of the data in plasma polymer field, the substrate temperature affects several surface processes (e.g adsorption, desorption, chemical sputtering) which strongly influence the layer properties [8-12]. Moreover, this also represents an important parameter reflecting the energy flux reaching the substrate by ionic bombardment, photon irradiation and surface reactions.

The present work aims to provide additional insight on the relation between the substrate temperature (T_s) and the atomic sulfur content (at.%S) of propanethiol plasma polymers (PTh-PPF). For this purpose, different experiments were carried out for identical plasma parameters in order to highlight the influence of T_s.

The PTh-PPFs were deposited from 1-propanethiol (99%, Sigma Aldrich) on previously cleaned 1x1 cm^2 silicon wafers following a procedure described elsewhere [5]. The depositions were carried out in a metallic vacuum chamber (65 cm length, 35cm diameter) where the plasma was sustained by a one-turn inductive Cu coil (10 cm in diameter). More details about the chamber description can be found in ref [5]. The coil was connected to an Advanced Energy radiofrequency (13,56 MHz) power supply via a matching network. The precursor flow rate, the working pressure and the power were kept constant at 10 sccm, 40 mTorr and 100 W, respectively. Two different distances between the coil and the substrate ($d_{S/C}$), were studied in this work, namely 5 and 10 cm. To assess the chemical composition of the layers, i*n-situ* XPS measurements were performed using a PHI 5000 VersaProbe apparatus. The substrate temperature was measured using a thermocouple in contact with the substrate holder through a screw. This parameter can be externally controlled by combining two independents heating and cooling systems.

First of all, the impact of the plasma discharge on the temporal evolution of the T_S as a function of T_s is measured (**Fig. 1**). As expected from the literature, in both cases after a given period of time, T_s reaches a plateau meaning that the loss and the gain of energy from the surface is equal [8, 13-15]. In our experimental window, T_s evolves from 30°C at low deposition time (t_d) to 90°C for higher t_d. [8]. As expected, at the same t_d, T_s is higher for the shorter $d_{S/C.}$ This is attributed to a higher ion flux and deposition rate (i.e exothermic surface reactions) at shorter distances form the coil. These data are compared with the evolution of the at.% S measured by XPS for different t_d. It can be learned that at low t_d, the films exhibit high sulfur content (~30%), even more than the precursor (25%); while increasing t_d results in a decrease in at.%S content until a plateau (~17%). The trend observed in the **Fig. 1** could be explained by considering our previous works on the propanethiol discharges [4, 5]. Mass spectra analyses reported in these studies disclosed a high production of H_2S [5]. Stable, these molecules can not take part to the growth of the layer but could be physisorbed at the growing film interface and embedded within nascent plasma polymeric matrix. This might explain the high sulfur content detected for short $t_{d.}$; hence low T_s. When increasing the deposition time, this physisorption process is likely limited by the T_s increasing. This leads to a decrease in the at. %S down to a stable value of ~17% that might correspond to the sulfur atoms chemically bonded in the plasma polymeric matrix.

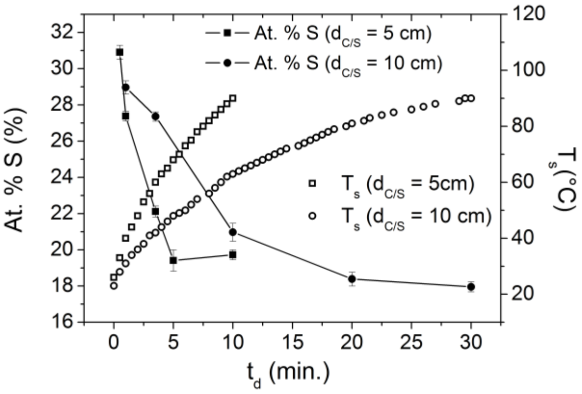

Fig.1 Evolution of at.%S as a function of td for $d_{S/C} = 10$ and 5 cm.

It should be emphasized that the evolution of the at.%S with t_d may be also related to the influence of the chemical composition of the substrate on the deposit properties at the early stage of the layer growth (i.e. for low t_d) [16]. In order to discard this hypothesis, a set of experiments were carried out for the two $d_{s/c}$ values by independently controlling T_s and t_d: i) at t_d = 1 min and T_s = 90°C (a T_s that corresponds to a long t_d in Fig.1) and ii) at t_d=30 min and T_s = 30°C (the T_s registered for a short deposition). The at.%S of the films is presented in **Fig.2** together with the data inferred from the experiments in which T_s was not externally controlled (cf. **Fig.1**). The examination of the data shows a good agreement between at.%S measured for equal T_s independently of the $d_{C/S}$ and the deposition time. These data validate unambiguously the effect of the T_s on the chemical composition of the Pth-PPF.

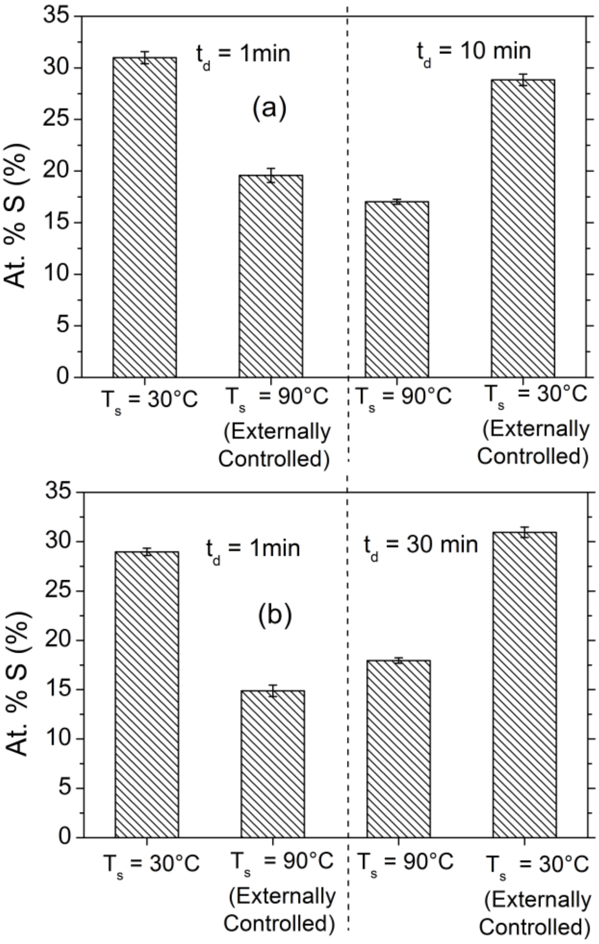

Fig.2 At.%S as a function of T_s and t_d for $d_{S/C}$ of (a) 10 and (b) 5 cm.

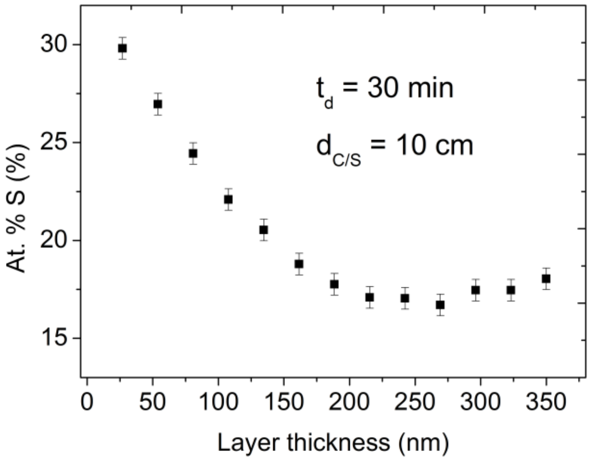

Fig.3 Chemical depth profile using C_{60}^+ gun for a layer synthesized for t_d = 30 min and $d_{C/S}$ = 10 cm.

As a complementary and supporting element, XPS depth profiles using a C_{60} ion gun (10k,10 nA) are performed for a layer synthesized at long t_d without controlling the T_s. As we can see in the **Fig. 3**, owing to the variation of T_s with time, heterogeneous chemical gradient in terms of sulfur content through the layer thickness can be generated. As expected, while increasing the thickness, the at.%S reaches a stable value.

The whole set of our data clearly demonstrate the influence of the T_s on the chemistry of propanethiol plasma polymer films. This result also proves that the deposition of homogenous PTh-PPF at this plasma conditions requires to accurately regulating the substrate temperature. In addition, the data herein reported pave the way for the fabrication of layers presenting variation of refractive index through the thickness [17].

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