# Establishment of a derivatization method to quantify 

## thiol function in sulfur-containing plasma polymer

## films

Damien Thiry ${ }^{{ }^{1 *}}$, Remy Francq ${ }^{1,2}$, Damien Cossement ${ }^{2}$, David Guerin ${ }^{3}$, Dominique Vuillaume ${ }^{3}$ and Rony Snyders ${ }^{1,2}$

(1) Chimie des Interactions Plasma Surface (ChIPS), CIRMAP, Université de Mons, 23 Place du Parc, B-7000 Mons, Belgium
(2) Materia Nova Research Center, Parc Initialis, B-7000 Mons, Belgium
(3) Molecular Nanostructures \& Devices" group, Institut d'Electronique, Microélectronique et Nanotechnologie (IEMN), Centre National de la Recherche Scientifique (CNRS), BP60069, avenue Poincaré, F-59652 cedex, Villeneuve d'Ascq, France


## Silicon <br> Oxygen

- Hydrogen

Sulfur
Nitrogen

Figure S1: Schematic description of a MPTS-SAM exhibiting a N-ethylmaleimide grafted at the sulfur extremity. The molecule geometry was optimized using MOPAC theoretical calculations (PM3 Optimization).


Figure S2: Schematic diagram of the minimal space between two N-ethylmaleimide molecules assimilated to cylinders.


Figure S3: Evolution of the [SH] (calculated using equation 2) measured by XPS and the normalized ToF-SIMS intensity of peak corresponding to $\left[\mathrm{C}_{6} \mathrm{H}_{8} \mathrm{NO}_{2} \mathrm{~S}\right]^{-}$as a function of $<\mathrm{P}>$. The errors bars correspond to the standard deviations calculated from XPS and ToF-SIMS measurements using different areas on the sample's surface. For all the experiments, the duration reaction was fixed to 86 h . This condition allows to reach a complete derivatization reaction.

The Table S1 collects the elemental composition of the Pr-PPF as-deposited and after the chemical derivatization reaction during 86h. This condition allows to reach a complete derivatization reaction.

| $\langle\mathrm{P}\rangle$ (W) | Pr-PPF as-deposited |  | Pr-PPF after CD during 86 h |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | \%C | \%S | \%C | \%S | \%O | \%N | [SH] |
| 14 | $50.22 \pm 0.05$ | $49.76 \pm 0.06$ | $57.12 \pm 0.25$ | $29.16 \pm 0.49$ | $11.51 \pm 0.13$ | 2.2 $\pm 0.53$ | $4.22 \pm 0.88$ |
| 38 | $64.42 \pm 0.52$ | $34.57 \pm 0.52$ | $65.43 \pm 1.7$ | 20.83 $\pm 0.41$ | $10.52 \pm 1.2$ | $2.49 \pm 0.27$ | $4.6 \pm 0.46$ |
| 100 | $71.44 \pm 0.6$ | $28.52 \pm 0.6$ | $64.73 \pm 1.54$ | $23.07 \pm 0.87$ | $9.55 \pm 1.73$ | $2.14 \pm 0.13$ | $4.13 \pm 0.31$ |

