

PO1015

The derivatization reactions of functional plasma polymers. Advantages and Limitations.

Anton Manakhov¹, Lenka Zajickova¹, Jean-Jacques Pireaux²

¹CEITEC-Masaryk University, Brno, Czech Republic ²University of Namur, Namur, Belgium

ant-manahov@ya.ru

The quantification of the density of various functional groups (amines, carboxyls, aldehyde, anhydrides) are often performed by gas phase or liquid phase chemical derivatization coupled with X-ray Photoelectron Spectroscopy (CD-XPS). This approach is very useful for the analysis of the plasma polymers, as the characterization of their branched structure by direct XPS measurement is often rife with many questions. The advantage of CD-XPS is the possibility to precisely measure the density of specific functional groups. Nowadays, the derivatization of various groups including carboxyl, primary amine, anhydrides is successfully established. However, researchers are often rife with the questions of the appropriateness of each methodology. The hardest discussions touch CD-XPS of primary amines using trifluoromethylbenzaldehyde (TFBA). To date the conclusion was that this method can be used for the characterization of amine films, although several side reactions could occur and might lead to overestimated NH₂ densities and this should be taken into account. Nevertheless, quite an important question related to the depth of the derivatization process was not studied before. Indeed, the depth of the derivatization reaction will depend on the porosity of the plasma polymer and the size of the reacting compound (e.g. TFBA).

In this work the depth of the reaction of TFBA with amine-rich cyclopropylamine plasma polymers was analysed by CD-XPS depth profiling. It was found that the reaction occurs only in the outermost surface (5-10 nm) and never in the bulk. In contrast, the trifluoroethylamine derivatization of anhydride groups in the maleic anhydride-acetylene plasma copolymers occurred at the entire depth of the sample. Hence, CD-XPS derivatization of primary amine by TFBA has one more limitation, i.e. low depth of the derivatization process which can be lower than the XPS analysis depth. Therefore it is important to take into account that the amount of NH₂ groups can be underestimated by TFBA derivatization unless the angular resolved XPS analysis is performed.

Keywords

Amine plasma
XPS
derivatization