

MODELING THE MULTILAYER STRUCTURE OF PLL-g-PEG ON Nb₂O₅ SURFACES

A.Rossi^{1,2}, L.Feuz¹, M.Textor¹, & N.D.Spencer¹

¹*Dept. of Materials, ETHZ, Zürich, Switzerland.* ²*Dept. of Inorganic and Analytical Chemistry, Università degli Studi di Cagliari, Cagliari, Italy.*

INTRODUCTION: The functionalization of metal oxide surfaces with adsorbed molecules allows the production of new tailor-made nanosized-bio-films. X-ray photoelectron spectroscopy allows the assessment of biocompatibility and the composition of the overlayer. So far the thickness of the layer can be determined using ellipsometry and angular-resolved XPS measurements, but both techniques have their limitations. In this study a novel approach to calculate the thickness of PLL and PEG layers was developed based on the XPS intensities of the spectra collected at only one emission angle. The first results obtained studying the influence of the molecular weight of the PEG chains are presented.

METHODS: A Physical Electronics 5700 X-ray photoelectron spectrometer was used to characterize the surface of niobium pentoxide surfaces before and after immersion in PLL(20)-[3.5]-PEG(x)². Measurement conditions are the same as those described in a previous paper².

RESULTS: C1s, O1s, N1s and Nb3d photoelectron spectra were resolved into surface and bulk components using parameters determined on the pure substances². All the spectra were multicomponent: the O1s peak at 531.5 ± 0.2 eV assigned to the oxygen of the PLL group NH-CH-CO contains also the contribution of niobium hydroxide and this contribution was taken into account for the quantitative analysis. The intensities of each component were used to calculate thickness and composition of the PLL and PEG layer^{3,4} simultaneously.

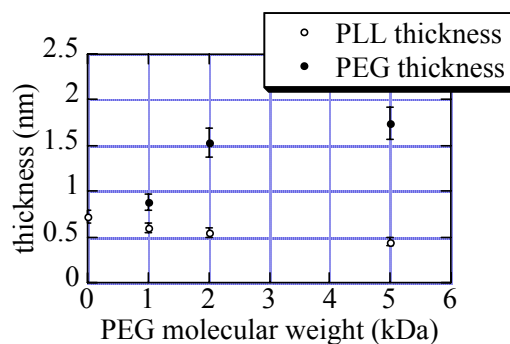


Fig. 1: PLL and PEG layer-thickness determined with the new model

DISCUSSION & CONCLUSIONS: XPS analysis of the films in this and previous work² has shown that binding-energy values for the different functional groups remain unchanged varying the PEG molecular weight. The intensity ratio of C1s to oxygen O1s in the (NH)C=O group is always lower than unity. This finding substantiates the assumption that the oxide substrate is hydroxylated. In agreement with the modified model (figure 2), a computer algorithm was written based on earlier work^{2,3,4}.

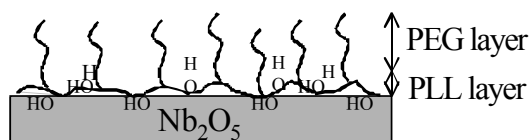


Fig. 2: Assembly of the PLL-g-PEG film on niobium pentoxide.

The results calculated with this model are in excellent agreement with the total thickness measurements obtained with ellipsometry. The three-layer model (fig. 1) provides clear evidence at high molecular weight of a deviation from a linear dependence of the PEG chain thickness.

In conclusion, the model applied in this study allows one to determine the thickness of both PLL and PEG layers, their sum being in agreement with ellipsometry. The model yields very good results for molecular weights of PEG up to 2kDa; the deviation at higher MW values requires further investigation.

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