SELF-ASSEMBLED MONOLAYERS OF ALKANEPHOSPHATES ON TITANIUM OXIDE SURFACES

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INTRODUCTION: Self-assembled monolayers of thiols on gold surfaces are widely used to produce model surfaces with well-defined chemical composition for a variety of applications including biomaterial and biosensor surfaces [1,2]. Alkane-phosphates and -phosphonates have been shown to form SAMs on a number of transition metal oxide surfaces such as titanium oxide (TiO_2), tantalum oxide (Ta_2O_5) and niobium oxide (Nb_2O_5) [3,4]. Using a combination of dedicated surface characterization techniques, the molecular structure of these adlayers has been demonstrated to be similar to thiols on gold with an intermolecular spacing of 5 Å (corresponding to 21 $Å^2$ per molecule) and a tilt angle of the molecular axis of 30–35° relative to the surface normal (Fig. 1). The binding of the phosphate head group to the metal oxide surface is believed to be through direct coordination between phosphate and metal cation and arguments have been given for the presence of both mono- and bi-dentate binding of the phosphate group thus enabling the formation of a close-packed layer.

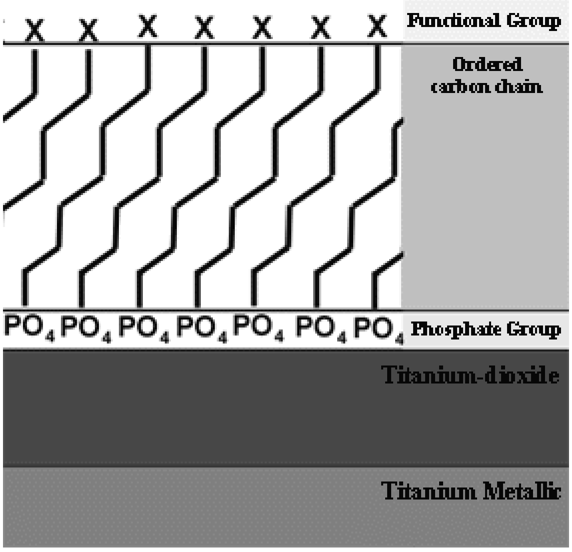

Fig. 1: Self-assembled monolayer of X-functionalized alkane phosphate on a titanium (oxide) surface

The use organic solvent solution to produce surface layers has clear disadvantages if the perspective is to use such techniques on an industrial scale. Moreover, for applications in areas such as medical devices and implants, the presence of even minor organic solvent residues in the adlayers may not be tolerated in view of potential cell-toxic effects and other biological risks. Therefore, a technique based on the deposition of SAMs from water-soluble alkylphosphate solutions has been developed and successfully applied to a variety of metal oxide substrates [5].

This paper descibes the application of methyl-terminated ("non-functionalized") and hydroxy-terminated dodecylphosphates ($DDPO_4$ and OH-$DDPO_4$ resp.) on flat/smooth titanium or titanium-oxide coated substrates as well as on rough (grit-blasted and acid-etched) titanium surfaces.

METHODS:

Substrates: Three different substrates were used: a) thin film of titanium dioxide (TiO_2) (20 nm) and b) titanium metal (100 nm) resp. deposited by physical vapor (PSI Villigen) onto silicon wafers or flat glass slides. c) Commercially pure (CP) titanium discs were grit-blasted and subsequently etched (received from Institut Straumann AG, Waldenburg).

Alkanephosphates and SAM formation: The used alkyl-phosphates molecules were prepared according to a previous publication [4,5]. The substrates were solvent cleaned and immersed for 48 hours in the aqueous amphiphile solution. The alkyl-phosphate and hydroxyalkyl-phosphate solutions were mixed in different ratios from 0 to 100 vol.-% with respect to the amount of OH-$DDPO_4(NH_4)_2$ at constant total phosphate concentration of 0.5 mM.

Contact angle Measurement: Surface wettability was investigated trough measuring advancing and receeding contact angle in a sessile water drop type of experiment. The measurements were performed in an automated way by stepwise increasing and decreasing respectively the water drop size.

RESULTS: Fig. 2 and 3 show the advancing and receeding contact angles of smooth titanium oxide surfaces and of structured SLA surfaces resp. after formation of a self-assembled monolayer from mixed aqueous solution of $DDPO_4$/OH-DDP O_4.

The contact angles depend on both the surface chemistry (composition of SAM) and the topography of the surface.

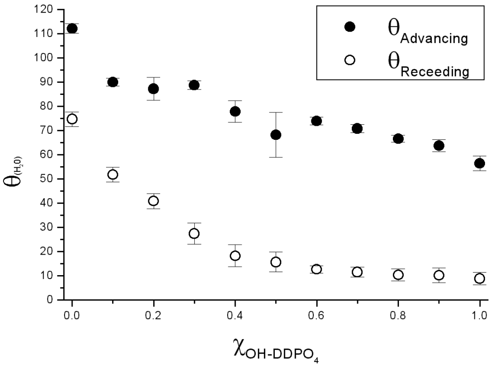

Fig. 2: Advancing and receeding contact angles of water on smooth titanium metal coated silicon wafer surfaces as a function of the the OH-$DDPO_4(NH_4)_2$ *concentration in the SAM forming solution, expressed as the mole fraction* $\chi_{OH\text{-}DDP04}$

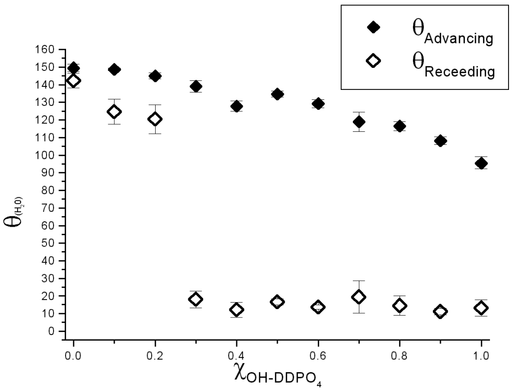

Fig. 3: Advancing and receeding contact angles of water on rough, particle blasted and acid etched (SLA) titanium metal surfaces as a function of he OH-$DDPO_4(NH_4)_2$ *concentration in the SAM forming solution, expressed as the mole fraction* $\chi_{OH\text{-}DDP04}$

The comparison between the experimental contact angles and model calculation based on equations given by Cassie [6] and by Israelatchvili and Gee [7] as well as detiled XPS analysis give evidence that the OH-$DDPO_4$ adsorbs somewhat preferentially leading to a ratio of OH-$DDPO_4$/$DDPO_4$ in the adlayer that is typically a factor of 1.4 higher than expected from the molar ratio in the aqueous amphiphile solution.

DISCUSSION & CONCLUSIONS: Alkanephosphates can be self-assembled from aqueous solution on titanium oxide surfaces to produce model surfaces with very well-controlled surface properties such as wettability. The technique is suitable to modify both flat/smooth surfaces and rough, highly structures surfaces. Such surfaces may have applications in the area of optical waveguide sensors (where transparent oxide-covered chips are used) and as model surfaces for cell–surface interactions. In the latter case, the possibility of independent control over the surface chemistry and the topography makes such systems particularly attractive for basic studies.

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