Application Note # 150

Organophosphonates Characterization Using MP-SPR

Phosphonic acids adsorption behavior was studied using Multi-Parametric Surface Plasmon Resonance (MP-SPR). Tetradecylphosphonic acid (TPA) adsorption onto differently treated gold surfaces was measured. Piranha and ammonia/hydrogenperoxide treatments were found to be the most optimal surface cleaning method for the SAM formation. TPA, vinylphosphonic acid (VPA), and octylphosphonic acid (OPA) adsorption onto the piranha treated surface was studied, and the thickness and the refractive index of the deposited layers were determined. The SAMs were 0.68 nm (VPA), 1.41 nm (OPA) and 1.73 nm (TPA) thick, which is in good agreement with the expected molecular length.

Introduction

Self-assembled monolayers (SAMs) are ordered layers formed spontaneously on solid substrates, and have played an important role in nanotechnologies for the last decades. Their ability to form well-defined monomolecular organic coatings creates new possibilities for various applications such as corrosion resistant surfaces, sensors, organic electronic devices, or adhesion promoters.

Phosphonic acid monolayers are able to produce stable, well-anchored thin layers on a variety of oxide surfaces for protection or adhesion purposes and for electronic device applications. Phosphonic acids are mainly used as complexing agents in detergents, as stabilizers for peroxides in the paper or textile industry and as corrosion inhibitors.

The unique MP-SPR instruments can perform measurements in a wide angular range (40-78 degrees) and at more than one wavelength, thus making the instrument an excellent tool for surface characterization. MP-SPR measures molecular adsorption in real-time. Same measurement also allows layer thicknesses to be calculated. Additionally, MP-SPR measures in air and in liquid without any change in the instrument setup, and the system is also compatible with a variety of organic liquids.

Materials and methods

Adsorption studies were performed using the BioNavis standard gold sensor slides. The best surface treatment procedure was determined by measuring tetradecylphosphonic acid (TPA) adsorption onto the sensor slides, pre-cleaned using one of the four cleaning methods:

a. O_2 –plasma (10 min at 100 W)

b. freshly generated ammonia/peroxide: NH_4OH (30%)/H_2O_2 (30%)/H_2O in a volume ratio of 1:1:5, for 10 min boiling at 80°C.

c. 2.5 M NaOH, immersion for 2 hours.

d. piranha solution (freshly prepared from sulfuric acid and hydrogen peroxide in a 3:1 volume ratio, immersion for 15 min.

After cleaning, slides were rinsed with MilliQ water and dried in a nitrogen stream prior to measurement.

Experiments were performed using the MP-SPR Navi™ 200 OTSO instrument. Vinylphosphonic (VPA 108 g/mol), octylphosphonic (OPA 194 g/mol), and tetra-decylphosphonic acid (TPA 278 g/mol) adsorption on piranha-treated gold sensor slides was followed *in situ* using the organophosphonates at a 5 mg/ml concentration in isopropanol, setting the flow rate to 100 µL/min and temperature to 25˚C (Figure 1).

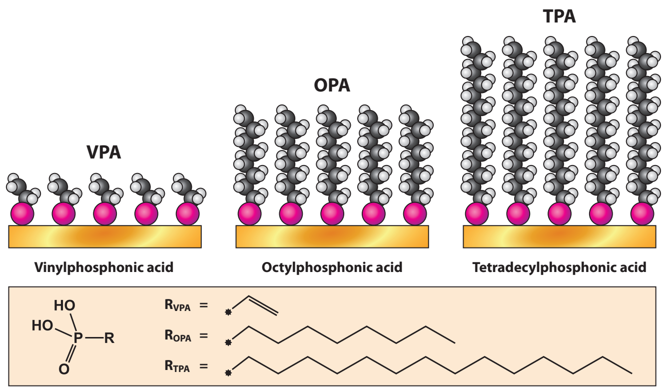

Figure 1. Various organophosphonates were measured using MP-SPR.

Results and discussion

TPA adsorption was minor onto non-cleaned gold surfaces and it was only slightly increased with O_2–plasma or 2.5 M NaOH treatment, whereas ammonia and piranha treatments created a much higher adsorption capacity (Figure 3). AFM pictures were acquired to check how surface treatments affected the surface morphology. As expected, more hazardous cleaning procedures created a rougher surface (Figure 2). However, morphology did not explain all the differences in the responses, because the amount of adsorbed TPA was the same for the roughest surface (piranha) and the smoother (ammonia treated) surface. Surface compositions were determined using XPS after treatment to exclude that oxidation or dissolution of silicates had affected the surface chemistry.

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All three organophosphonates adsorbed similarly to the piranha treated surfaces. The thickness of SAM layers were determined from the MP-SPR responses separately for both wavelengths with the two media method (see AN#128), using measurements in air and in isopropanol. The monolayer thicknesses are in good agreement with the calculated lengths of the stretched molecules. However, the TPA layer thickness is slightly smaller than estimated (Figure 4). Most likely, the longer alkyl chains of TPA are slightly bent on the surfaces, resulting a lower thickness of the SAMs.

The organophosphonic acids can be removed from the gold surfaces simply by rinsing with water, indicating a rather weak binding. However, a simple tempering step for 1 h at 90 °C leads to molecules becoming irreversibly attached to the gold surface.

Conclusions

MP-SPR is proven to be an excellent real-time label-free tool for SAM adsorption studies. Sensitive MP-SPR is suitable even for the detection of small molecular weight compounds, such as organophosphonic acids. MP-SPR measurements can be performed in air or in organic solvents without any change in the instrument setup, which makes the MP-SPR a versatile tool for layer characterization. MP-SPR provides thickness and refractive index values even for monolayers, showing its sensitivity. Thickness information can be used to ensure a proper conformation of the adsorbed molecules on the surface.

See in more detail how to measure layer thickness and refractive index using MP-SPR in Application Note #128.

References:

Original article:

Niegelhell et al. Langmuir 2016, 32, 1550-1559

Recommended instrumentation for reference assay experiments
MP-SPR Navi™ 220A NAALI, 210A VASA, or 200 OTSO with additional wavelength (L)
Sensor surfaces: Au, other metal or inorganic coating
Software: MP-SPR Navi™ Control, DataViewer, LayerSolver™

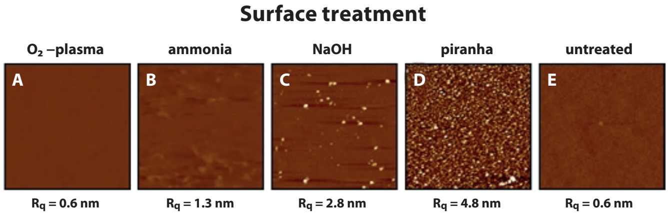

Figure 2. AFM pictures after surface treatments reveal differences in roughness of the surface. More stronger cleaning procedures created a rougher surface as expected. R_q is surface roughness determined by AFM. Image size is 10 × 10 µm.

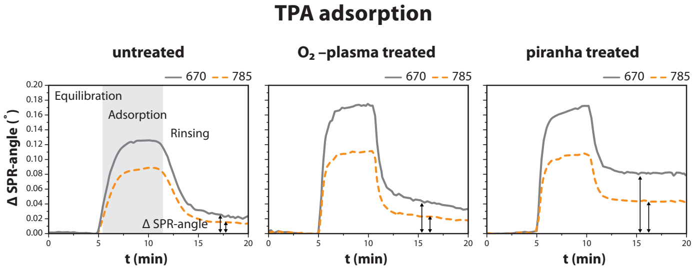

Figure 3. Tetradecylphophonic acid (TPA) adsorbed only slightly onto the untreated gold surface, adsorption was slightly better to the O_2 plasma and NaOH treated surfaces, however, piranha and ammonia treated surfaces were clearly more favourable for the adsorption.

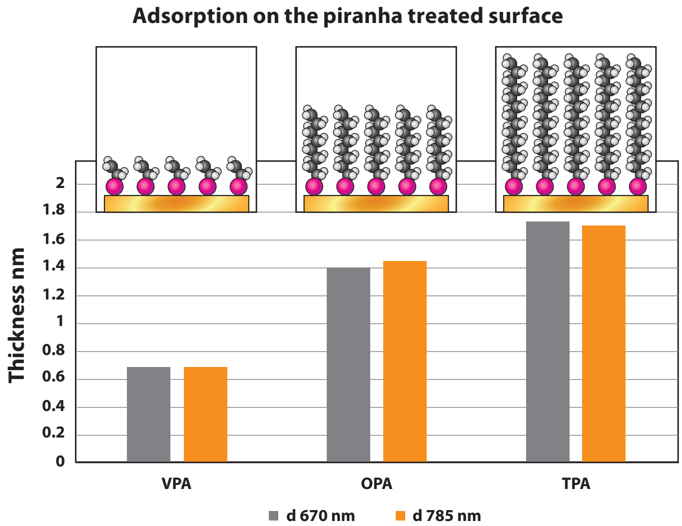

Figure 4. SAM thicknesses: vinylphosphonic (VPA), octylphosphonic (OPA), and tetradecylphosphonic acid (TPA).

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e-mail : info@bionavis.com
www.bionavis.com