Self-assembly of phosphonic acid layers on the oxide of aluminium

Tom Hauffman, T. Breugelmans, Y. Van Ingelgem, E. Tourwé, H. Terryn, A. Hubin
Department of Electrochemical and Surface Engineering, Vrije Universiteit Brussel,
Pleinlaan 2, 1050 Brussels

Introduction
Self-assembling monolayers find their applications in a broad range of areas: biosensors, conversion layers, nano-electronics, light emitting organic devices,... The best known system in the field is the adsorption of thiols on gold. However, the range of organic functionalities which can be deposited on gold substrates is rather limited and gold itself is not generally industrially relevant. Therefore, interest has shifted in the last decades towards other substrates such as oxides.
A very interesting system in this scientific field is the adsorption of phosphonic acids on aluminium oxides. Not only the possibility of the formation of such self-assembling monolayers on an oxide substrate opens up the industrial possible applications, but also the fact that low length molecules can be deposited from an aqueous solution.
In this study we present the ex and in situ study of the deposition of self-assembling n-octylphosphonic acid layers on pretreated aluminium oxide layers from water and ethanol. The adsorption mechanisms are unraveled using a set of complementary surface analysis and electrochemical techniques: AFM, XPS, VISE and odd random phase multisine electrochemical impedance spectroscopy.

Experimental
N-octylphosphonic acid is purchased from Alfa Aesar (purity 98%) and used as received. The aluminium samples are pretreated as described in a previous paper [1,2]. AFM analysis is performed using a CPII apparatus from VEECO. XPS analysis is carried out using a PHI1600 equipment. Visual ellipsometry spectra are obtained with a XE100 from Woollam.
The impedance spectra are acquired using a two-electrode set-up. The counter electrode is a platinum grid. The electrolyte consists of a 0.1M $NaClO_4(.H_2O)$ ethanolic solution. The concentration of n-octylphosphonic acid is 1 mM. The perturbation signal applied is a 10 mV RMS variation around the open circuit potential. The impedance spectrum is acquired between 0.1 and 10^4 Hz.

Results and Discussion
1. Adsorption of n-octylphosphonic acid molecules from water
An ex situ analysis is performed using XPS and AFM. Here, it is observed that throughout submersion time, molecules tend to continuously assemble on the surface forming islands. The Stranski Krastanov–like behaviour is confirmed using in situ AFM and in situ VISE analysis. The layer growth as observed by elipsometry is shown in figure 1.
It is characterised that the layers do not only assemble island-wise but that the growth mechanism can be separated in three steps: growth of the number of islands, coalesence of the existing islands, growth of the islands' in height. The mechanism observed can be seen in figure 2. It is assumed that the polarity of the solvent is the main driving force for this behaviour. Therefore, ethanol, being less polar than water, seems a more suitable choice for the self-assembly of phosphonic acids on aluminium oxide.
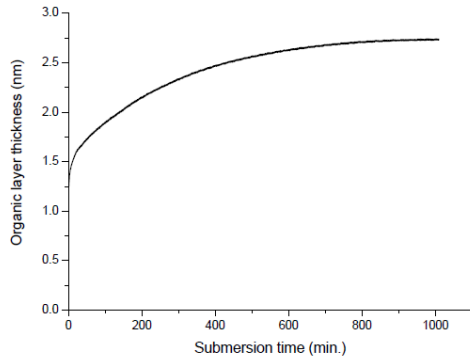
Figure 1: Organic layer growth on aluminium oxide as observed in situ with visual ellipsometry
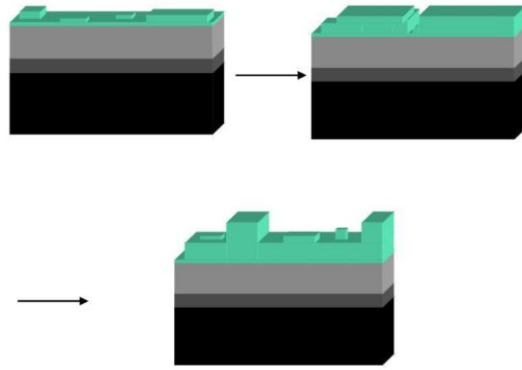

Figure 2: Adsorption mechanism of n-octylphosphonic acid from water

2. Adsorption of n-octylphosphonic acid molecules from ethanol

The Bode plots acquired throughout immersion time of the pretreated aluminium oxide sample in a 1mM n-octylphosphonic acid ethanolic solution will be shown. There is a clear change in behavior after 24 hours of immersion time. SEM imaging (figure 3) shows that the oxide surface blisters and is thus deteriorating.
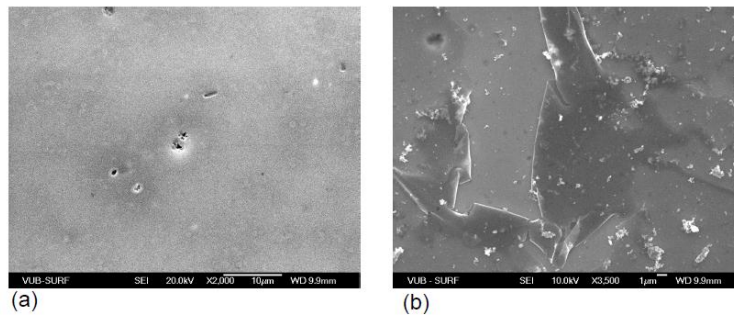

Figure 3: SEM images of the blank oxide surface (a) and the oxide surface after corrosion (b)

This is only possible when a corrosive environment is present. This environment can only be there due to the combination of water (supporting electrolyte and expelled from the reaction between phosphonic acids and the aluminium hydroxyls), which tends to stay nearby the hydrophilic surface. N-octylphosphonic acids can dissolve in this water, possibly creating an environment with a pH lower than 3.

These observations and reasoning lead to the model presented in figure 4 to fit the data.
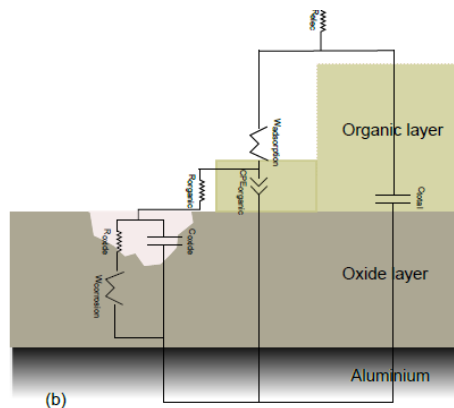

Figure 4: model to fit the adsorption of n-octylphosphonic acids on aluminium oxide from ethanol. Relec = electrolyte resistance, Ctotal = total capacitance of the adsorbed organic layer and the underlying oxide, Wadsorption = Warburg element due to the reaction between the phosphonic acid molecules and the oxide,

Radsorption = the corresponding electron transfer resistance, CPEorganic and Rorganic = the adsorbing organic layer, Coxide and Roxide = the non covered oxide layer, Wcorrosion = Warburg element due to corrosion reaction

It could be statistically shown, by a comparison of the noise levels observed and the residuals between fit and experiments obtained that the model is suitable to model the system under investigation. The fitted data will be presented for every model parameter. As such, three time frames can be defined from these parameter trends. In the first time frame (between 0 and 20 hours of immersion time), the phosphonic acids adsorb on the surface and local corrosion is going on. In a second time frame (between 24 and 36 hours of immersion), corrosion breaks through, removing partially the organic layer and the oxide surface. Hereafter, a recovery of the organic layer is obtained combined with ongoing corrosion reactions.

3. Complementary ex situ surface analysis techniques

As ORP MS EIS is an indirect analysis technique, requiring intensive modeling, and as a supporting electrolyte is involved when performing impedance measurements, it is necessary to confirm the electrochemical results by a set of complementary analysis techniques [4]. This has been done using AFM, XPS and VISE. It could be shown by all techniques that the organic layer deposition is very unstable. AFM (figure 5) shows holes in the surface, which univocally can be coupled with the deterioration of the oxide. XPS and VISE measurements show clearly that the adsorbed layer is unstable and that there is a loss in thickness of the oxide film.
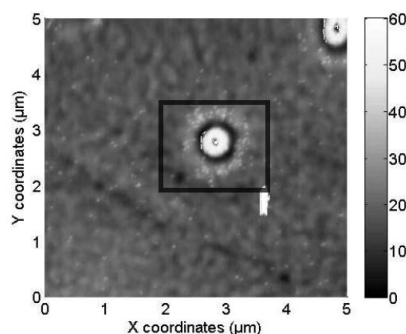

Figure 5: Typical AFM image of n-octylphosphonic acid molecules on aluminium oxides from ethanol

Conclusions

In this study, it is established that n-octylphosphonic acid never will form a SAM on aluminium oxides when deposited from a solvent. Polar solvents give rise to multilayers and less polar solvents trigger corrosion reactions at the surface. A methodology for thin film research and mechanism characterisation is presented in this study.

Acknowledgements

References

1. T. Hauffman, O. Blajiev, J. Snauwaert, C. Van Haesendonck, A. Hubin, H. Terryn, Langmuir 24 (2008) 13450.
2. T. Hauffman, L. Van Lokeren, R. Willem, A. Hubin, H. Terryn, Langmuir 28 (2012) 9317.
3. T. Hauffman, T. Breugelmans, Y. Van Ingelgem, E. Tourwé, H. Terryn, A. Hubin, Electroch. Comm. 22 (2012) 124.
4. T. Hauffman, A. Hubin, H. Terryn, Surf. Int. Anal. accepted for publication.