

In situ monitoring of ultra slow oxide growth on copper protected by a self assembled monolayer

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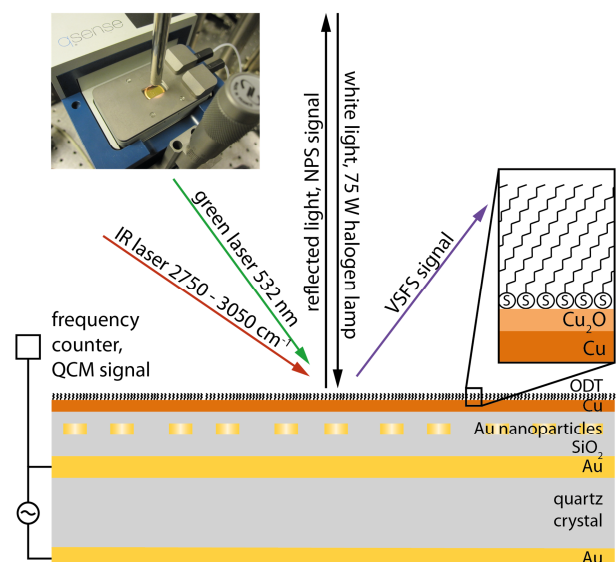
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The need for in situ monitoring of very slow growth of oxides or other corrosion products on metals is obvious in different kinds of applications, ranging from the corrosion of electronic materials to corrosion monitoring in industrial field applications.

In the present study the initial stages of atmospheric corrosion of copper covered with a self assembled monolayer of octadecanethiol (ODT) was investigated in situ with a multi analytical approach including three ultrasensitive state-of-the-art techniques. The molecular structure and conformation of ODT was evaluated using an inherently interface sensitive technique, vibrational sum frequency spectroscopy (VSFS). It allows the detection of the formation of thin oxides on the copper surface and the simultaneous structural changes in the hydrocarbon chains of ODT.¹ To quantify the amount of oxide formed, a mass sensitive technique, the quartz crystal microbalance (QCM), was combined with VSFS.² Both VSFS and QCM data analysis is based on the assumption of homogeneously distributed corrosion products on the copper surface. However, it is well known that the oxidation and corrosion processes often occur heterogeneously. Hence, integration of VSFS-QCM with another photon based surface sensitive technique, nano plasmonic sensing (NPS),³ enabled us to distinguish homogeneous and heterogeneous corrosion under in situ conditions. Furthermore, NPS possesses a time resolution of the order of seconds, which makes it a good candidate to study relatively fast corrosion processes.

Cathodic reduction was also used as a complementary technique to detect and quantify the corrosion products formed on the samples after exposure.

In the presence of oxygen in the atmosphere a thin oxide layer is formed due to penetration of oxygen molecules through defects in the ODT monolayer and reaction with the copper surface. Formation of this oxide layer changes the non-resonant part of the VSFS signal, due to changes in the electronic properties of the interfacial regime. This change in the non-resonant part of the VSFS signal could be correlated to the mass obtained with QCM as well as with the data achieved by NPS. A very good agreement between the three techniques was achieved. This unique combination of three in situ techniques facilitates the study of different corrosion systems where interfacial changes in electronic and optical properties as well as changes in mass occur. The sensitivity of the techniques under current exposure conditions corresponds to 20% of an oxide monolayer for VSFS, 2.5% for QCM and 1.2% for NPS.



A schematic depiction of the combined QCM-D and INPS sensor, serving also as the VSFS sample.

References:

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