Real-time monitoring of metal stripping and deposition with EC-MP-SPR

Multi-Parametric Surface Plasmon Resonance (MP-SPR) enables combined electrochemical and SPR measurements (EC-MP-SPR). In this study, MP-SPR was utilized to follow real-time copper deposition and stripping processes under constant current (galvanostatic) conditions. Process of deposition of copper in terms of layer thickness (d), refractive index (n) and absorption coefficient (k) was determined with dedicated LayerSolver™ software.

Introduction

The Surface Plasmon Resonance (SPR), phenomenon more commonly utilized in biochemical interaction characterization, is extremely sensitive to thin layers having plasmonic properties, including most transition and noble metals. Multi-Parametric SPR (MP-SPR) measures the intensity of the reflected light for a wide range of angles at multiple wavelengths, and can be used as an extremely sensitive thickness characterization tool for metals as well as soft materials.

MP-SPR can be equipped with an electrochemistry cuvette (EC) which enables monitoring of surface changes such as growth or removal of a metal film during imported electric potential changes. The BioNavis EC cuvette cell is equipped with internal reference and counter electrodes for reliable measurement.

Electrochemistry coupled to SPR (EC-MP-SPR) is very useful for following the elementary processes of electrodeposition and stripping of metals. The MP-SPR with amperometric and coulometric methods enables the properties of the formed layers to be followed in real-time, and further analysis allows the thickness and optical constants to be determined.

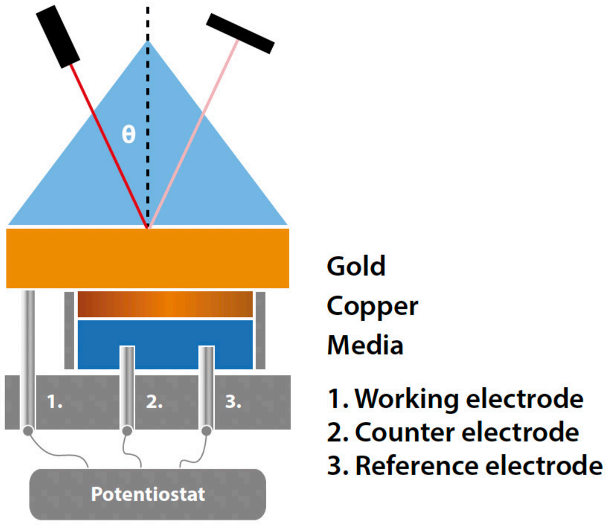

Figure 1. MP-SPR – EC setup. Copper deposition and stripping processes were monitored in real-time.

Materials and methods

Measurement was performed *in situ* using an MP-SPR-Navi™ 200 OTSO instrument. A Palmsens3 potentiostat was employed for galvanostatic deposition of copper onto a clean gold surface during the MP-SPR measurement (Fig.1). The deposition was performed using a 0.1 M $CuSO_4$ solution in 0,1 M HCl. A flow rate of 100 µL/min was maintained, and after recording one minute of baseline in angular scan mode an oxidation current of 50 µA was applied by the potentiostat. Deposition was followed for 2.5 minutes.

Data were processed by the MP-SPR Navi™ LayerSolver™ to elucidate the deposited copper layer optical constants (n, k) and thickness (d). Gold sensor slide optical constants and thicknesses were fitted with background values for the calculation.

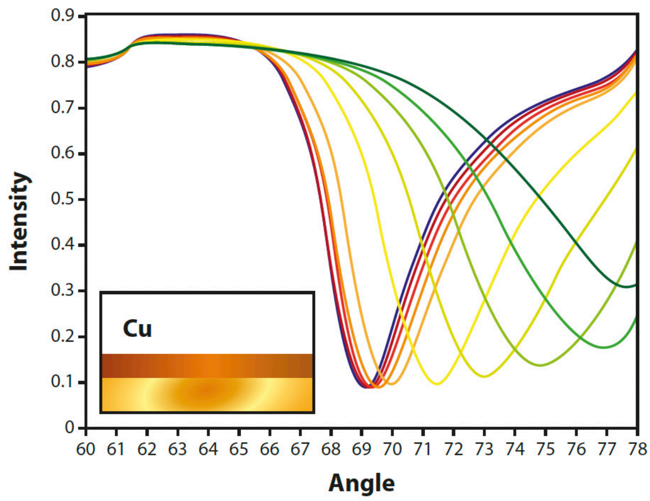

Figure 2. MP-SPR curves for the deposition of copper, measured at 670 nm wavelength for 2.5 minutes.

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Results and discussion

In the measurements the SPR peak minimum intensity shifted upwards and the peak showed significant broadening with respect to time due to copper deposition (Fig.2). The response was indicative of a slightly inhomogeneous, possibly rough layer building up on the surface of the gold. The measurement was performed on two separate spots on the surface. The optical constants and thickness were found to match in both measurement spots. The corresponding changes of layer thickness are plotted in Fig.3.

In this particular case, the SPR shift was mainly dominated by the growth of a dielectric absorbing layer with optical constants very different from those of copper. Theoretically, the optical constants of copper are very similar to those of gold. However, it is likely that the copper surface does not grow regularly, and the data then show deposition of copper intermediates or copper nanoparticles, which have a rather high refractive index and absorption coefficient (Popov *et al*. 2016).

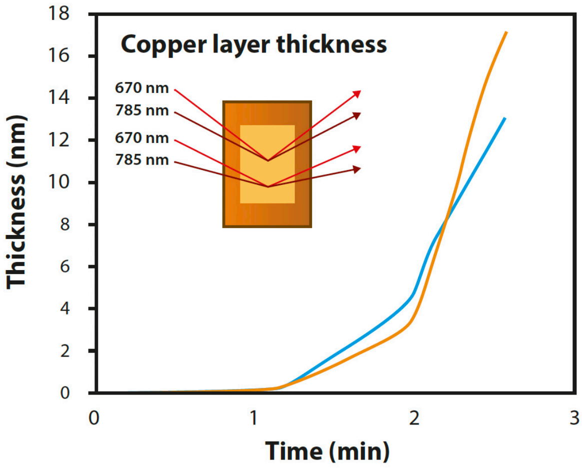

Figure 3. Copper layer thicknesses from two different measurement spots on the sensor surface calculated by LayerSolver™. Upper spot (blue) and lower spot (orange) curve. Calculated optical constants of copper deposit. Refractive index (n) and extinction coefficient (k) are shown in the insert.

Conclusions

A potentiostat can be combined with MP-SPR, and surface changes during electric potential changes can be monitored in real time, such as metal deposition and stripping processes. Galvanostatic experiments allow monitoring the regular coating of metals onto a clean gold surface, and the kinetics of growth can be followed. Advanced LayerSolver™ software can be used to determine the optical constants and thickness of deposited layer.

Reference:

Popov *et al.*, Morphology of Electrochemically and Chemically Deposited Metals, Springer, 2016

Recommended instrumentation for reference assay experiments

MP-SPR Navi™ 200 OTSO or 210A VASA equipped with electrochemistry flow cell SPR321-EC

Sensor surface: Au

Software: MP-SPR Navi™ Controller, DataViewer, and LayerSolver™ for MP-SPR Navi™

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