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Real Time In-Situ ellipsometric and gravimetric monitoring for electrochemistry experiments

R Beck, L. Broch, Nicolas Stein, L. Johann

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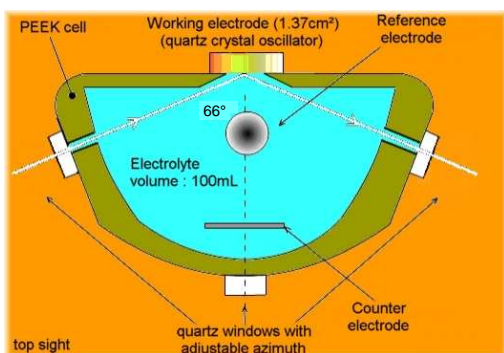
This work describes a new system, which uses real time spectroscopic ellipsometer with simultaneous electrochemical measurements and Electrochemical Quartz Crystal Microbalance (EQCM) measurements. This method is particularly adapted to characterize electrolyte/substrate interfaces during electrochemical and chemical processes in liquid medium.

Electrochemical Quartz Crystal Microbalance

- ⇒ 5MHz quartz cristal oscillator
 - ⇒ Precision of 20ng.cm⁻²
 - ⇒ Mass variation every 160ms
 - Sauerbrey relation**
 - ⇒ Resonance frequency of the quartz crystal is linked to the change mass of the electrode
 - ⇒ Calibrated $K = 37.28\text{Hz} \cdot \mu\text{g}^{-1}$
- $$\Delta f = -K\Delta m$$

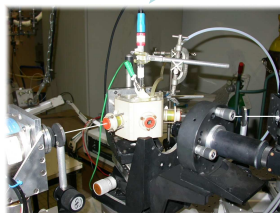
Ellipsometry

- ⇒ Based on Jobin-Yvon ellipsometer
- ⇒ Real time (full spectrum of Ψ - Δ every 25ms)
- ⇒ Rotating Compensator Ellipsometer type
- ⇒ Achromatic optical elements
- ⇒ Jobin-Yvon CP 140 spectrograph with multichannel detector.
- ⇒ Xenon light source



Potentiostat galvanostat

- ⇒ Radiometer PGP201
- ⇒ Stationary polarization modes :
 - potentiodynamic,
 - galvanodynamic,
 - potentiostatic and
 - galvanodynamic.
- ⇒ Time acquisition = 100ms



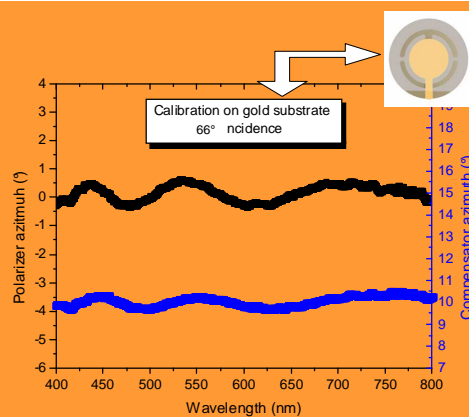
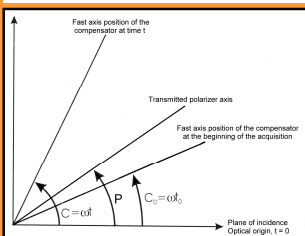
Data acquisition is synchronized by a specially dedicated program.

Spectroscopic calibration

Ellipsometric measurements with 25ms sampling time are only achievable with a fixed analyzer position ($A=45^\circ$). Thus it is impossible to measure a spectrum of Ψ - Δ with a two-zone technique to correct systematics errors. Therefore the ellipsometer calibration is extremely important for high precision measurements and we propose a spectroscopic calibration (i.e. determination of the azimuth of elements according to the wavelength) on the whole spectral range.

The detected photocurrent has the form :
 $I = \alpha_0 + \alpha_{2c} \cos 2(\omega t - C_0) + \alpha_{2s} \sin 2(\omega t - C_0) + \alpha_{4c} \cos 4(\omega t - C_0) + \alpha_{4s} \sin 4(\omega t - C_0)$
 where ωt is the azimuth of the fast axis of the compensator.
 The appropriate Fourier coefficients are measured using Hadamard transform.

First, we adopted residual calibration for the analyzer. Secondly, three positions of the analyzer ($A=0^\circ, 45^\circ$ and -45°) are used for determining transmitted polarizer axis (P) and the fast axis of the compensator (C_0) as a function of wavelength.



Application

Analysis of the Electrodeposition and Stripping of copper thin Films

⇒ Electrochemical reference system exhibiting 100% faradic efficiency

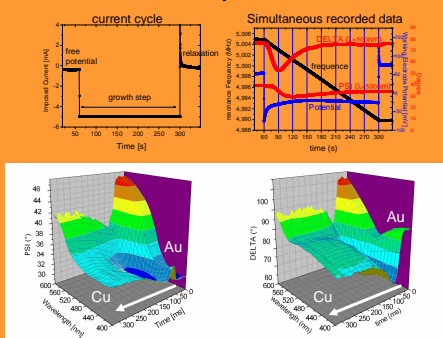
Experimental conditions :

- Acidic medium $[\text{H}_2\text{SO}_4] = 0.5\text{M}$
- Sulfate copper $[\text{CuSO}_4] = 0.085\text{M}$
- Counter electrode : copper disc
- Reference electrode $\text{AgCl}/\text{Ag}^\circ$ sat. deaerated electrolyte

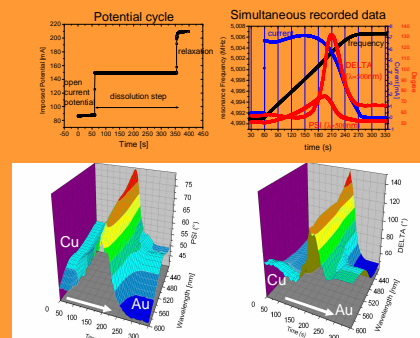
Spectral range :

Due the strong absorbance of the electrolyte in the 600-800nm range, the spectral range of the study was restricted to 400-600nm

Growth process



Stripping process



Complete reversibility of the growth/stripping process
 Different optical path of the film formation and the dissolution step

We developed a powerful tool to investigate in situ electrode processes in liquid medium in the 100 ms time range. This system allowed complete description of the evolution of the electrochemical interface through in situ, simultaneously and synchronized records of gravimetric (resonance frequency), thermodynamic (Potential), coulometric (current) and optical data (delta and psi spectra). The evolution of the surface electrode can be described from complementary information between mass evolution (EQCM), coulometric and film optical parameters (SE). Very short sampling times can exhibit transient phenomena of the electrochemical interface.

