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Operando Spectroscopic Ellipsometry Probing Electrochemical Interfaces

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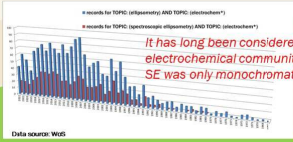
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Spectroscopic Ellipsometry (SE) is a non-invasive, non-destructive, and contactless optical technique which is based on the change in the polarization state of light as it is reflected from a surface. Among other instrumentations for in situ and operando experimentation, the technique can particularly be promoted as an analytical tool to diagnose solid-liquid interfaces. Besides other pioneer groups, our former heads Profs. Jean-Marie LECUIRE[†] & Roland KLEIM[†] initiated investigations [1] dedicated to *in situ* electrode processes in liquid medium leading to the complete description of the evolution of an electrochemical interface through *in situ*, simultaneously and synchronized records of coulometric, optical and gravimetric data [2].

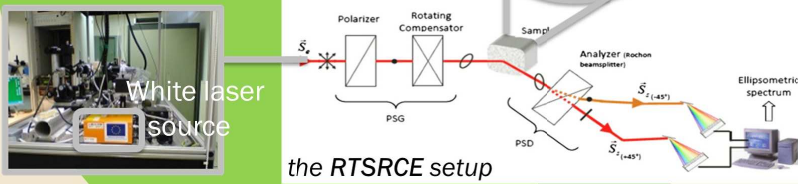


The resulting current setup is a home-made real-time spectroscopic ellipsometer with rotating compensator (RTSRCE), operating in the visible spectral range at a signal acquisition rate of 25 ms, with simultaneous electrochemical measurements (potentiostat apparatus, 30 ms), and optionally in surplus combinable gravimetric measurement (electrochemical quartz crystal microbalance EQCM probe, 160 ms). Last instrumental upgrades concerned the elimination of systematic ellipsometer errors and the use of a supercontinuum white laser as source [3,4].

Different configurations are possible. Working Electrodes consist e.g. of a clamped bare substrate...



home-made coupling cells

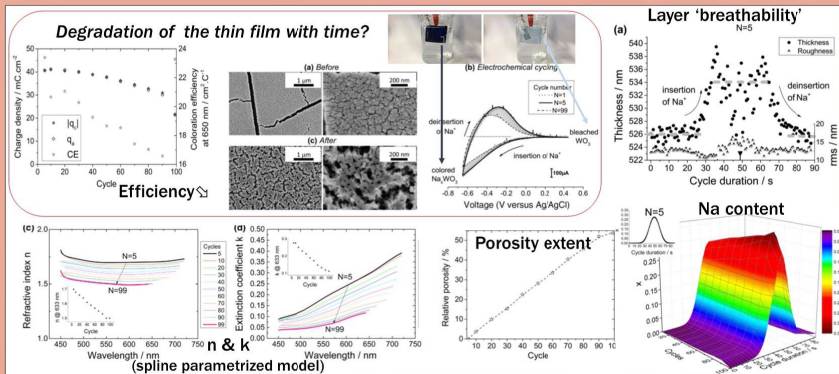


the RTSRCE setup

This fruitful co-development has given rise to several joint PhDs and research periods over three decades. To illustrate the opportunity of the proposed coupling for possible new incomers, some recent materials and operation conditions will be briefly exposed covering three different wet process applications:

Ageing process of chromogenic coatings

Example of the electrochromic sputtered a-WO_{3-x} during 99 (de)sodiation cycles

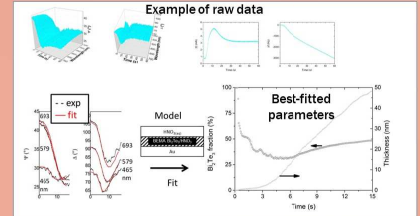


A lot of properties of interest is accessible to help to explain the observed attenuation [7]:

- A progressive water uptake appears the main reason and provokes also a slight Na increase.

Electrocrystallization process

Example of the growth mechanism of chalcogenide Bi₂Te₃ electrodeposition



The joint analysis of the data (SE, CA, EQCM) yields to propose a step-by-step-scenario of the very early fifteen seconds stages of this process: [5]

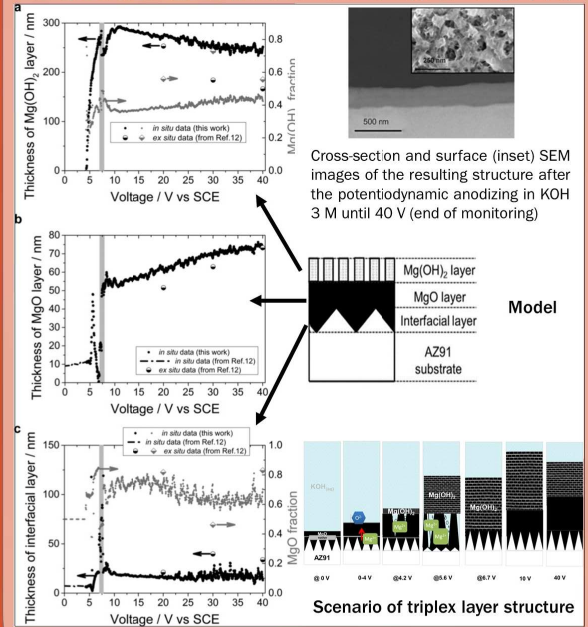
- Induction time (350 ms)
- Under Potential Deposition formation of Te (0.35-3 s)
- Growth of Three Dimensional Crystallites (3-11.5 s)
- Coalescence (>11.5 s)



Anodization process of light metals

Example of the pre-sparking regime of plasma electrolytic oxidation of Mg AZ91D alloy

The monitoring reveals the fine morphological characteristics of the multilayered passivated structure from 0 to 40 V-applied voltage: [4, 6]



- First compact MgO layer (0.4 nm/s) until the electrochemical breakdown and precipitation of a porous Mg(OH)₂, which acts as a protective membrane and under which a very defective new MgO anodic layer repassivates (0.7 nm/s) probably responsible of the low dielectric breakdown (μ-arc initiation)

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SCAN ME

