

Quantitative determination of adsorbates and charge accumulation with spectroscopic ellipsometry

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Currently considerable effort is put on improving the microscopic understanding of electro-chemical surface reactions. The key functionality is usually determined by atomic scale structural, chemical and physical properties of the solid-liquid interfaces. Unfortunately, most of the surface sensitive techniques, which are successfully used in UHV, cannot be applied in liquid environments. Only electro-chemical scanning tunneling microscopy (EC-STM) [1] and almost ambient pressure XPS are useable exceptions. Other obvious approaches are using optical methods in the transparency spectral range of either the electrode or the electrolyte.

In the presented work we demonstrate the extremely high surface sensitivity of spectroscopic ellipsometry, which can be used to gain also quantitative information on the amount of surface adsorbates[1] and- to our knowledge for the first time- **the charge accumulation at metal electrodes**[2]. NIR-NUV ellipsometry is combined with results of conventional cyclic voltammetry (CV) (Fig. a), impedance spectroscopy, and EC-STM (Fig. c,d) in order to study the surface of crystalline metal electrodes in-situ and quasi in-operando. As an example the ellipsometric angle Delta is plotted (in Fig. b) in comparison to CV for the copper (110) or (111) surfaces in HCl solution. A particular attention is drawn to catalytic electrochemical process like the hydrogen evolution reaction (indicated by A'), where the overall transferred charge, as determined by CV, cannot be used to achieve information about respective surface changes. The latter reaction is actually studied intensively since decades but the fundamentals of the catalytic process are still controversially discussed.

For Cu(111) we found by means of the in-situ measurements evidence for an adsorbed densified water layer at the surface. The ellipsometric measurements disclose, in addition, a cationic adsorbate in connection with the hydrogen evolution reaction, which is interpreted as a protonation of the adsorbed water layer or the surface. The obtained results imply furthermore an inhibiting effect of the adsorbate with respect to the hydrogen evolution reaction.

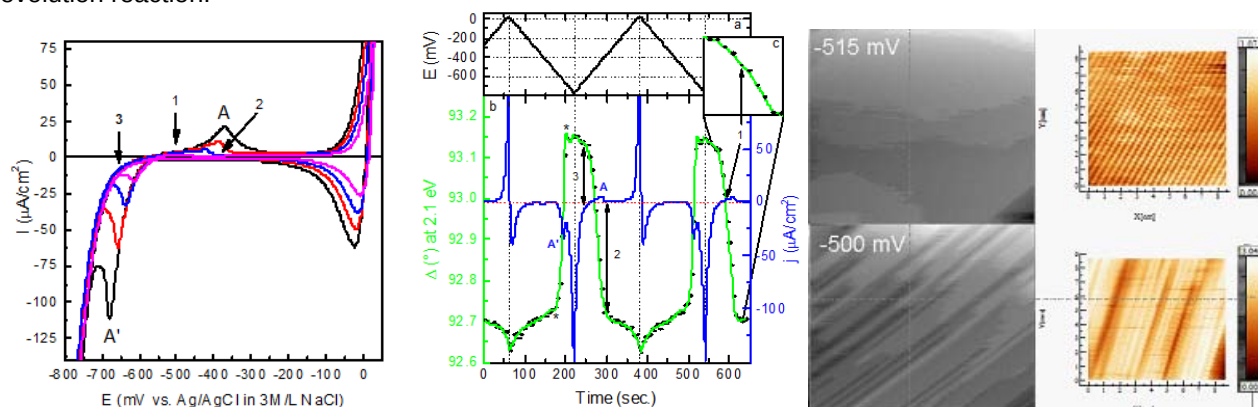


Fig. a) Cyclovoltammetry of the Cu(110) surface. Fig b) (spectroscopic) ellipsometry transients for different electrochemical potentials, Fig. c) ECSTM images at two different potentials (89 x 89 nm); Fig. d) ECSTM achieves atomic resolution (9 x 9 nm, height bar top 1.07Å, height bar bottom 3.04 Å).

References

- [1] G. Barati et al, Langmuir **30**, 14486–14493 (2014)
- [2] submitted to Langmuir