

# DFT study for halide covered Ag(100) and Au(100) surfaces in an electrochemical environment

Alexandra C. Dávila<sup>1</sup>, Lukas Deuchler<sup>1</sup>, Svenja Hövelmann<sup>1</sup>, Eckhard Pehlke<sup>1</sup>

<sup>1</sup> *Institut für Theoretische Physik und Astrophysik,  
Christian-Albrechts-Universität zu Kiel, Germany*

Nanoscale processes determining the growth dynamics and the film roughening during metal electrodeposition are an active experimental, as well as theoretical, research field. As observed by Ruge *et al.* [1] and Krug *et al.* [2] for Au/Au(100) homoepitaxy in an electrolyte with  $\text{Cl}^-$  ions, the growth dynamics depend on the electrode potential. Prerequisite to study electrochemical processes on the surface is the knowledge of the dependence of anion chemical potential on sample voltage. In general this relation is derived from thermodynamics [3,4], following the concept of the computational hydrogen electrode. Here we address its accuracy by studying the halide coverage as a function of sample voltage, and comparing to experimentally observed structures. The cyclic voltammogram of Au(100) in HCl solution [5] evidences the lift of Au(100)-hex reconstruction and the halide adlayer phase transition as a function of sample potential, for I/Au(100) see [6]. Halogen (Cl, Br, and I) adsorption on Ag(100), and Au(100) surfaces has been investigated using density functional calculations, carried out with PWscf from the Quantum ESPRESSO package [7]. Our DFT simulations include incommensurate adsorbate reconstructions, which are simulated in a large unit cell with coverages  $\Theta = 0.46, 0.65$ , as well as Au(100)-hex reconstruction with small or zero halide coverage. Differences occur between the range of experimental and theoretical sample voltage where the experimentally observed reconstructions are stable. In particular, for the Cl/Au(100) system, we obtain a shift of 350 mV with respect to experiment. By means of experimental results [5], a corrected (shifted) scale of the electrode potential is proposed for the Cl/Au(100) system. With reference to the shifted sample voltage scale, the atomic structure of the boundary between  $c(2 \times 2)$ -Cl adsorption domains on the unreconstructed Au(100) surface have been calculated and are compared to STM images from [8].

- [1] M. Ruge *et al.*, Phys. Rev. Lett. **112**, 055503 (2014)
- [2] K. Krug, J. Stettner, O. M. Magnussen, Phys. Rev. Lett. **96**, 246101 (2006)
- [3] J. K. Nørskov *et al.*, J. Phys. Chem. B **110**, (2006)
- [4] I. T. McCrum, S. A. Akhade, M. J. Janik, Electrochim. Acta **173**, (2015)
- [5] A. Cuesta, D. M. Kolb, Surf. Sci. **465**, (2000)
- [6] X. Gao *et al.*, J. Phys. Chem. **98**, (1994)
- [7] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009)
- [8] Y.- C. Yang, K. Hecker, O. M. Magnussen, Electrochim. Acta **112**, (2013)