

Voltohmometry – an Alternative Detection Principle at Ultrathin Metal Electrodes in Solution
Hendrik Emons¹, Olaf Glueck, Michael J. Schoening²
Research Center Juelich, Germany

¹Institute of Applied Physical Chemistry, ²Institute of Layers and Interfaces, D-52425 Juelich, Germany

A new electrochemical detection principle is described for the trace analysis of dissolved species which can be deposited at polycrystalline thin-film metal electrodes and which change the surface resistance of the electrode. Because the latter parameter is measured in dependence on the applied electrode potential we call this method voltohmometry in analogy to the well-established term voltammetry for registering current-potential curves.

It is known for many years that the lateral dc resistance of a very thin metal film can depend on the adsorption or deposition of atoms and molecules on its surface [1]. But this phenomenon has not been exploited until now systematically for analytical determinations of species in solution. First attempts for the measurement of deposited heavy metals by following the change of surface resistance in dependence on the applied potential at single crystal silver electrodes have been reported by Hanewinkel et al. [2] but the application of such single crystal electrodes seems to be not favorable for practical applications. Moreover, an efficient mass production of the required electrode structures would be necessary for the introduction and widespread use of a new electrochemical principle into analytical laboratories.

A major prerequisite for significant contributions of the surface resistance to the measuring signal in a specially designed measuring system represents the preparation of very smooth metal layers of a few nanometer thickness. This working electrode as the most critical part of the experimental set-up has been prepared by using silicon planar technology. At present the actual working electrode material exposed to the measuring solution consists of a polycrystalline gold layer. Silicon wafers are used as starting material. The patterning of the metal structures was achieved by optical lithography. After the first lithographic step the thin-film electrodes were deposited by electron beam evaporation under high vacuum conditions. For stabilizing the 15-20 nm gold layer on silicon a 5 nm thick polycrystalline chromium layer served as adhesion promoter between the silicon substrate and the gold layer. In a second lithographic step following metallization the conducting tracks were thickened up to 200 nm. Finally the whole wafer with exception of the thin-film electrodes and the bond pads was covered with an electrically insulating polyimide layer.

The principles of voltohmometry will be explained and illustrated by measurements of the deposition and dissolution of various species at the ultrathin working electrodes. Corresponding experimental developments including the measuring system and specially designed batch as well as flow-through cells will be presented.

For exploiting the capabilities of voltohmometry for analytical purposes we have performed a number of initial experiments. After securing the reversibility - and consequently the reproducibility of the resistance-potential measurements at home-made working electrodes - the potential use of stripping procedures with this detection principle has been tested. It has been shown that the determination of heavy metals at the trace level can be realized with linear sweep voltohmometry and limits of detection in the range of a few $\mu\text{g/L}$ have been obtained for Cd^{2+} and Pb^{2+} with cyclic voltohmometry at 1-10 mV/s [3]. Tl^+ could also be determined down to 20 $\mu\text{g/L}$ by this approach. In analogy to anodic stripping voltammetry one can achieve a certain selectivity by appropriate selection of the accumulation potential and various metal ions can be analyzed simultaneously if their stripping potentials differ by at least 150 mV.

The present opportunities and limitations of voltohmometry will be discussed. This includes the chemical stability of the microstructured working electrode arrangements and the drift of the background resistance of this nanometer-thin electrodes during electrochemical measurements in solution. It will be shown that the first analytical investigations are promising from the point of the further exploitation of this alternative detection principle. The resistance changes can be measured with high sensitivity and accuracy which allows the

application of voltohmometry for trace analysis. It is expected that the limits of detection can be significantly lowered by developing appropriate procedures for stripping voltohmometry in solutions with convective mass transfer. Finally, further developments of voltohmometry are envisaged.

- [1] E.H. Sondheimer, *Advan. Phys.* 1 (1952) 1-42
- [2] C. Hanewinkel, H. Winkes, D. Schumacher, A. Otto, *Electrochim. Acta* 42 (1997) 3345-3349
- [3] O. Glueck, M.J. Schoening, H. Lueth, A. Otto, H. Emons, *Electrochim. Acta* 44 (1999) 3761-3768