Oscillating Tunneling Barriers at the Solid / Liquid Interface

M. Hugelmann, P. Hugelmann, and W. Schindler

Institut für Hochfrequenztechnik und Quantenelektronik
Universität Karlsruhe (TH)
Kaiserstrasse 12, 76131 Karlsruhe (Germany)

Scanning Probe Microscopy (SPM) at the solid / liquid interface is widely used to investigate metal clusters and films on foreign substrate surfaces [1,2]. Usually, the vertical calibration of heights is done using known height variations, preferably substrate steps.
Of special interest in such investigations is the height of the first monatomic layer on the foreign substrate. The values published for such layers by various groups are not in agreement, which was also found in recent investigations in our group [3,4]. Due to the change of the imaged metal while scanning a foreign metal step edge the principle question arises, whether different metals have different effective barrier heights in the electrochemical environment.

Here we present very precise measurements of the effective barrier height under electrochemical conditions. Basically Distance Tunneling Spectroscopy (DTS) was used to determine the dependence of the tunneling current on the STM-tip / substrate distance. For an increase in accuracy a very detailed, sophisticated measurement and evaluation technique was applied. It was possible to perform very fast measurements due to the high bandwidth of the used system. Thermal drift was avoided by measuring times of 50 ms for each complete DTS characteristic.

With this procedure we investigated the effective barrier heights of Au and Pb. To avoid asymmetries due to different workfunctions of different metals the procedure was applied in systems where the substrate and the STM tip are from the same metal. The experiments have been performed in ultrapure, deaerated 20mM $HClO_4$ solution. A flame annealed gold single crystal was used as substrate, and as STM tip an etched gold wire was utilized. Experiments at Pb-Pb tunneling barriers were carried out by adding 1mM $Pb(ClO_4)_2$ to the electrolyte, to grow electrochemically a thin lead film on the substrate and on the STM tip. The electrochemical working electrodes, STM tip and substrate, have been operated with a BP-600 bipotentiostat (EC-Tec). The galvanically isolated STM tip current output of BP-600 has been fed into a Nanoscope E STM electronic (Digital Instruments).

We find an oscillating dependence between tunneling barrier and distance. The fact that this behavior can be found in both systems let us conclude that the correlation between current and distance in the electrochemical scanning tunneling microscopy reflects mainly the electronic nature of the electrochemical interface.
From previous investigations and simulations it is well known that ordered layers of water molecules on metal surfaces have a separation of around 0.3 nm [5]. The observed oscillations in the tunneling barrier are discussed in view of the structural data available in the literature.

References:

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