

Advanced Scanning Probe Instrumentation for Electrochemical Nanotechnology

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At present, electrochemistry offers the unique possibility to fabricate and to study the properties of well-defined nanostructures showing lateral widths of less than 20 nm.

Whereas vapour phase based lithographic preparation techniques of nanostructures suffer from the preparation induced generation of irreversible modifications or defects, electrochemical methods allow to fabricate "as grown" structures without such preparation induced defects [1,2]. In particular, scanning probe (SPM) techniques have been shown to be useful in the electrodeposition of metal structures with such small lateral widths at predefined substrate positions [1-7].

However, our own experience from the recent years shows, that the experimental requirements for preparation and investigation of nanostructures by SPM techniques are much higher than the requirements for the investigation of laterally extended film growth which has been intensively studied by SPM techniques [8].

There are basically two problems resulting from the combination of electrochemistry and scanning probe microscopy: The bipotentiostat and the electrochemical cell. In contrast to the features of the widely used commercial electrochemical SPM equipment, the application of *in situ* SPM techniques during growth and investigation of nanostructures requires the SPM tip to be a regular electrochemical electrode which can be controlled independently of the substrate [2]. The potentials of both substrate and SPM tip must be controlled very precisely. Even potential and current transients, for example due to shortcuts while scanning, have to be resolved. The current resolution at the SPM tip must be dramatically increased compared to the commercial systems resolution limits of 10 – 30 pA in order to be able to study deposition and dissolution processes of structures which are consisting of only 10000 or even less atoms. The tunneling currents during SPM imaging have to be reduced below several pA in order to scan the surfaces without changing the surface structure by the scanning process itself. Rapid potential changes at the SPM tip or/and at the substrate are required to initiate electrochemical processes. The slew rate of these (potentiostatic) pulses must be in the μ s range which requires bandwidths of the bipotentiostats of MHz.

The electrolyte must be completely deoxygenated in order to avoid parasitic reactions at any electrode, which is an essential requirement during serious studies at semiconducting (for example silicon) surfaces. The electrodes in the electrochemical cell must be in a properly set up three electrode geometry.

Thus, we have built an universal measurement system, consisting of a bipotentiostat and an electrochemical cell,

which provides electrochemical facilities at the highest level combined with *in situ* SPM techniques. The system allows the additional *in situ* application of optical techniques like magneto-optical Kerr effect measurements or electro-optic sampling using fs laser pulses. In contrast to commercial systems, our bipotentiostat has been implemented neither as a software program nor software controlled, but rather in hardware which improves the performance dramatically.

Our bipotentiostat operates the electrochemical cell independently of the SPM measurement system. Thus, we are able to use any SPM measurement system, and we are not restricted to the commercial suppliers of so called electrochemical SPM. The bipotentiostat features two working electrode channels which can be operated using internal or external current/voltage converters. This allows to use specific converters of very high current resolution and of lowest noise level as close to the electrode as possible, as well as to connect SPM scanners with the tip as a regular electrochemical electrode. The bandwidth of each channel is in the MHz range, and allows the modulation with up to two external signals or pulses down to sub- μ s duration. The electrode potential is actually measured by very high slew rate amplifiers, avoiding deviations from the setpoint of the electrode potential due to the electrode capacitance, modulation pulse duration, or other effects. The output of each working electrode channel can be fed into subsequently connected electronics like lock-in amplifiers, or especially into the independently running SPM measurement system in order to record scanning probe images with a tunneling current resolution down to fA.

This bipotentiostat operates an electrochemical cell providing a volume of approximately 250 ml of electrolyte, which can be *in situ* deoxygenated. Oxygen concentrations can be *in situ* monitored to a level as low as 0.1 ppb. The SPM head is mounted on a special flange which can be inserted into the cell. Laser beams are introduced into the cell by additional flanges, and can be simultaneously applied while scanning with the SPM. The cell fits in between the pole shoes of an electromagnet allowing investigations in magnetic fields.

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