

Detection of Copper with Potentiostatically Controlled Microcantilever Sensors

Gilbert M. Brown,* Fang Tian, Jianhong Pei, David L. Hedden, and Thomas Thundat
Oak Ridge National Laboratory
PO Box 2008, Oak Ridge, TN 378231-6119

Micromechanical cantilevers used in atomic force microscopy (AFM) have been used for a variety of applications beyond surface imaging. Prominent among these applications is the use of these devices as a platform for the development of chemical and biological sensors based on the bending-plate principle. When molecular adsorption is confined to one surface of a microcantilever, it decreases the surface free energy. When the spring constant of a microcantilever is of the same magnitude as the free energy change due to surface adsorption on it, the microcantilever will undergo deflection due to the adsorption-induced stress. The deflection of the microcantilever can be measured with subnanometer sensitivity using the methods developed for AFM including optical, piezoresistive, capacitance, and piezoelectric detection methods. Although microcantilever sensors can be operated in air, vacuum, or liquid, we have been particularly interested in the development of sensors for metal ions in the environment. The damping effect in a liquid medium, however, reduces the resonance response of a microcantilever sensors or acoustic wave devices. The bending response of a microcantilever sensor device, however, remains unaffected by the presence of a liquid medium

Microcantilever-based sensors have been shown to be extremely sensitive, however commercially available silicon AFM microcantilevers coated on one surface with gold do not have any particular chemical selectivity, particularly in solution. Chemical selectivity has been achieved by coating one side of the microcantilevers with a selective film such as a SAM of an alkane thiol having a head group suitable for molecular recognition. Selective coatings have been developed for sensing Cr(VI), Cs⁺, Hg²⁺, Ca²⁺, and H⁺, and work is in progress to develop coatings that are selective for Cu²⁺, TcO₄⁻, and Sr²⁺. The use of controlled potential electrochemical techniques, however, offers a simple means of achieving chemical selectivity by controlling the potentials at which oxidation and reduction occur. In this paper we have investigated the deposition and anodic stripping of Cu²⁺ in aqueous solution.

Commercial rectangular silicon microcantilevers (Contact silicon tipless cantilever, MikroMasch USA) having dimensions 350 μm long, 35 μm wide, and 1 μm thick were used. One side of the whole chip was first coated by depositing a 5-nm layer of chromium followed by a 30-nm layer of gold. Clear finger nail polish was used to cover the gold-coated microcantilever chip and conductive wire of the chip holder, so that only the microcantilever was exposed in the electrolyte solution. A scanning probe microscopy (SPM) system with electrochemical cell supply (picoSPM 2500, Molecular Imaging, MI) was employed to control the electrochemical potential and to measure cantilever deflection. Electrochemical control was maintained by using a standard three-electrode potentiostat with a silver

wire as the reference electrode and a platinum wire as the counter electrode. The bending of the microcantilever was measured by monitoring the position of a laser beam reflected from the back (uncoated silicon side) of the cantilever onto a four-quadrant photodiode.

Surface free energy density can be represented by surface stress in the Suttleworth equation

$$\sigma = \gamma + \partial\gamma/\partial\varepsilon \quad (1)$$

where σ is the surface stress, γ is the surface free energy, and ε is the elastic surface strain (the latter of which is usually small and can be ignored). The radius of curvature and the adsorption-induced surface stress on the microcantilever can be related using Stoney's formula with the result that deflection is proportional to surface stress. An understanding of the dependence of surface stress on charge and potential at the solid-electrolyte interface will lead to a better understanding of processes occurring at an electrified interface. The Gibbs-Duhem equation for an interface can be written as

$$d\gamma = -qdE - \sum_i \Gamma_i d\mu_i + (\sigma - \gamma)d\varepsilon \quad (2)$$

where E is the electrode potential, q is the surface charge, Γ_i is the surface excess of species I, μ_i is the chemical potential of species I, and the other symbols have been previously defined, and this equation provides a relationship between surface free energy, surface coverage, and stress. This equation can be differentiated with respect to potential to obtain the generalized Lippman equation that allows the derivative of deflection with respect to potential to be related to the surface charge during a deposition or stripping process.

Microcantilevers coated with gold have been used as the working electrodes on which copper has been deposited and stripped off in different concentrations of Cu²⁺ in a 0.1 M NaNO₃ supporting electrolyte. Microcantilever deflection and the first derivative of deflection with respect to potential were measured during both the deposition and stripping cycles. The potential was held at -0.4 V vs Ag QRE for 300 sec and the stripping sweep was at 20 mV/s. Our results indicate that microcantilever bending can be used to detect Cu(II) at a threshold of 10⁻¹¹ M. The derivative of deflection has a peak at roughly the same potential as the stripping peak, but the deflection measurement can be seen at three orders of magnitude lower concentration than the current measurements. The stripping peak can be used to identify the presence of copper in solution in the same way that current peak is used in voltammetric measurements.

Acknowledgement. This research was supported by the DOE Office of Biological and Environmental Research (OBER) and Environmental Management Science Program (EMSP). Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the US Department of Energy under contract number DE-AC05-0096OR22725.

* Contact Information: phone 865-576-2756; fax 865-574-4939; email brownm1@ornl.gov