Supporting Information for: Nanowire probes for high resolution combined scanning electrochemical microscopy – atomic force microscopy

1. Thermal Oxidation of Silicon Probes

Silicon AFM probes (Force Modulation MULTI75 Lot Oriel) were thermally oxidised dry in a 1 inch tube furnace oven on a quartz boat under an O_2 flow of 200 standard cubic centimetres per minute (sccm) for a total of 9 hours (3 runs for 3 hours) at 1100 ^{o}C. Oxidised probes were cooled slowly under oxygen between runs. Gas flow rates were accurately controlled using mass flow controllers. Figure 1 shows a FE-SEM cross section image clearly showing the 460 nm thick thermal oxide film which provides a pin-hole free insulating layer on the silicon. Cyclic voltammetry (Figure 2) performed on an oxidised cantilever in a solution containing 10 mM $IrCl_6^{3-}$ and 0.1 M KNO_3, displayed only very low capacitive currents, indicating a well-insulated film.

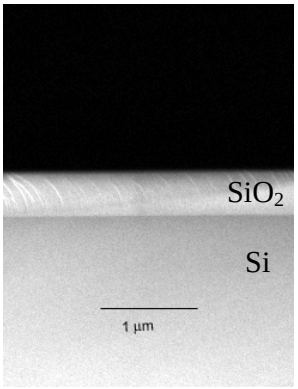

Figure 1. FE-SEM cross-section image of a thermally oxidised silicon AFM probe.

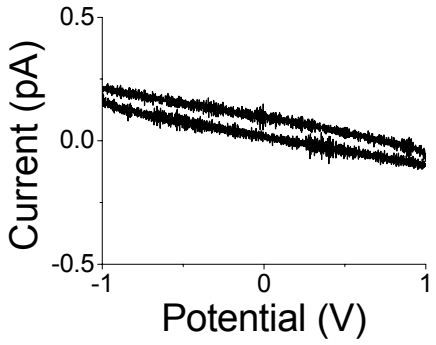

Figure 2. Cyclic voltammogram recorded in a solution containing 10 mM $IrCl_6^{3-}$ and 0.1 M KNO_3 at a scan rate of 20 mV s^{-1}, using a silicon AFM probe (FESP, L. O. T. –Oriel Gmbh & Co.) which had been thermally oxidised for 3 hours by the procedure described above, as the working electrode. An Ag/AgCl reference electrode was employed.

2. Poly(oxyphenylene) Insulation Layer

A thin conformal poly(oxyphenylene) film was formed on the Au-coated single walled carbon nanotube bundle AFM tip by the electropolymerisation of a 1:1 methanol:water-based monomer solution containing 60 mM phenol, 90 mM 2-allylphenol and 160 mM 2-n-butoxyethanol. The solution pH was adjusted to 9.2 by the drop wise addition of ammonium hydroxide and used on the same day as preparation. Electropolymerization was conducted at a potential of +2.5 V against a silver wire quasi-reference electrode (AgQRE) for 20 minutes. The probe was positioned so that the tip apex faced the reference electrode. The probe was carefully rinsed in a 1:1 methanol:water solution immediately after electrodeposition. The copolymer film was subsequently heat cured at 150 ^{o}C for 30 minutes to form a pinhole free insulating layer.

3. Silicon Nitride Insulation Layer

Silicon nitride was deposited on either side of the probe, which served as a protective layer to prevent salt damage and prolong the lifetime and stability of the probe.

Silicon nitride films were deposited on the insulated nanowire probes using a room-temperature deposition technique, namely inductively coupled plasma chemical vapor deposition (ICP CVD)

employing SiH_4/N_2 (NH_3 free: Plasmalab System 100 ICP180 from Oxford Instruments Plasma Technology).

4. Focused Ion Beam (FIB) Cutting

Focused ion beam milling was achieved using a FEI Strata FIB200TEM system. During probe alignment, prior to nanowire cutting, single scans were used with a low beam current to minimize damage to the insulating layer. The insulated nanowire was cut using a beam current of ~ 10 pA. Care was taken to ensure a good electrical contact between the probe and the FIB sample holder, to minimised local charging at the tip apex.

5. Topographical Imaging with the nanoelectrode probes:

To demonstrate the high topographic resolution possible with the nanowire based SECM-AFM probes, a 1 μm square height image of evaporated Au on a silicon substrate was recorded (Figure 3). The image was taken in tapping mode, in air (height scale 15 nm).

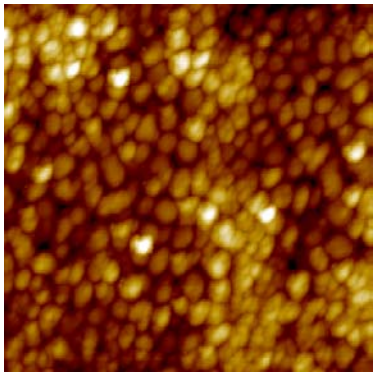

Figure 3. 1 μm square height image of Au on a silicon substrate (15 nm height scale).