

Cleaning and Surface Activation of Microfabricated Interdigitated Microsensor Electrodes (IMEs), Planar Metal Electrodes (PMEs), Independently Addressable Microband Electrodes (IAMEs), and E'Chem "Cell-On-A-Chip".

An ABTECH Application Note

Anthony Guiseppi-Elie, Sc.D.

President and Scientific Director

ABTECH Scientific, Inc., 911 East Leigh Street, G24, Richmond, Virginia, 23219 USA

<http://www.abtechsci.com>; abtech@abtechsci.com; Tel. 804 783 7829; Fax. 804 783 7830

I. INTRODUCTION

Cleaning and surface activation procedures are summarized for interdigitated microsensor electrodes (IMEs), planar metal electrodes (PMEs), independently addressable microband electrodes (IAMEs), and co-planar electrochemical "cell-on-a-chip" devices. These electrodes and sensor devices are all quite similar in that they are all produced via state of the industry microelectronics fabrication procedures (microfabrication). These procedures may involve thin film conductor (metal or oxide, such as indium-tin oxide, ITO) deposition, microlithographic patterning, chemical vapor deposition and packaging. Where appropriate, these electrodes and devices possess line and space features that are on the order of microns. The metallization on these devices typically comprise an adhesion promotion layer of 100 Å titanium-tungsten alloy (Ti-W) that resides between the substrate and the desired metal. The desired metal layer is typically 1,000 Å gold (Au), platinum (Pt), palladium (Pd) or silver (Ag). These metallic layers are generally prepared by magnetron sputtering or by e-gun deposition. Several different metals may be exposed on a single chip, such as in the microelectrochemical "cell-on-a-chip" device. Such a device may possess either platinum, gold or palladium and silver. The device may also possess a silicon nitride (Si_3N_4) topcoat layer that passivates the busses but provides a window through which the active area of the electrodes are exposed or the functional area of the device is accessed. This application note summarizes cleaning procedures for these various electrodes and devices. It emphasizes wet chemical, UV-ozone, and plasma cleaning procedures where appropriate and takes into account the delicate features on these devices. This application note also addresses activation of these various device surfaces. While cleaning removes organic, inorganic and ionic species not native to the surface, activation goes beyond cleaning as it seeks to introduce a uniform, atomic composition and structure at the near surface. Hence activation may strive to produce a uniform concentration of hydroxyls on an activated glass or a thin uniform oxide on gold or platinum. Activation may also strive to remove any native oxide on Au or Pt and produce a uniform metallic surface.

CAUTION: *The following procedures involve the use of highly caustic, acidic and noxious chemicals. These procedures may produce vapors that may irritate mucus membranes and cause burns to exposed skin. These procedures should only be performed while wearing appropriate protective safety apparel, in a properly vented fume hood, and under the supervision of a qualified chemist.*

II. SURFACE CLEANING PROCEDURES

A. Standard Wash for Grease and Solvent Removal

This general degreasing procedure is performed in sequence and without much delay between each step. This procedure is useful in removing finger grease, adventitious organic deposits and most general processing, machine, and/or cutting oils.

- a) Immerse in boiling trichloroethylene (TCE) for 1 min.
- b) Immerse in boiling acetone for 1 min.
- c) Ultrasonicate in isopropyl alcohol (2-propanol) for 1 min.
- d) Wash in flowing DI water for 1 min.
- e) Dry in a filtered nitrogen stream.

B. Removal of Residual Organic/Ionic Contamination

This procedure removes trace organics, physically adsorbed monolayers of adventitious organics (e.g. self assembled organic layers that are not “covalently bonded” to the surface, such as alkane thiols and silane layers) and some chemically adsorbed monolayers of organics that are NOT removable by Procedure A.

- a) Immerse in a (5:1:1) solution of $\text{H}_2\text{O} : \text{NH}_4\text{OH} : \text{H}_2\text{O}_2$ that is maintained at 75 – 80 °C. Hold for 10 s.
- b) Immediately quench the solution under running DI water for 1 min.
- c) Wash in DI water for 5 min.

C. Hydrous Oxide Removal (for silicon substrates only)

This procedure chemically etches a thin layer of silicon oxide and exposes a fresh silicon oxide surface. This procedure may also be used to activate silicon oxide surfaces, producing an abundance of free hydroxyls, for further chemical derivatization via covalent coupling.

- a) Immerse in a (1:50) solution of $\text{HF} : \text{H}_2\text{O}$ for 10 sec.
- b) Wash in running DI water with agitation for 30 sec.

D. Heavy Metal Clean

This procedure aims at removal of heavy metal ions that may exist as traces adsorbed to the metal or metal oxide surface.

- a) Immerse in a (6:1:1) solution of $\text{H}_2\text{O} : \text{HCl} : \text{H}_2\text{O}_2$ that is maintained at 75 – 80 °C. Hold for 5 min.
- b) Quench the solution under running DI water for 1 min.
- c) Wash in DI water for 5 min.

E. UV-Ozone Clean

This procedure removes monomolecular layers of chemically bound organics on metallic and oxide surfaces. Chemisorbed and covalently bound self-assembled monolayers of adventitious organics, alkane thiols, and silane layers may be removed using this procedure. This method removes organics that are NOT removed by Procedures A and B above. This procedure is NOT suited to thick (micron level) organic films.

- a) Clean as in Procedures A and B above. Then clean the device(s) for 10 – 25 min in the UV_Clean UV/Ozone cleaner to remove adventitious adsorbed organics.
- b) Wash the UV-cleaned IME device by ultrasonic washing for 1 min. in 2-propanol.
- c) Dry the device in an air-filtered convection oven at 80 °C for 30 min to 1 hour to remove traces of surface bound water.

F. Plasma Clean

This procedure removes thick (micron level) films of various organic materials including photoresists. An oxygen (O_2) or argon (Ar) plasma is suitable for most organic films. Plasma cleaning has been shown by AFM to cause some roughening of evaporated and sputter-deposited gold surfaces.

- a) Plasma etch for a time determined by the thickness of the film.
- b) Wash the plasma-cleaned IME device by ultrasonic washing for 1 min. in 2-propanol.
- c) Dry the device in an air-filtered convection oven at 80 °C for 1 hour to remove traces of surface bound water.

G. Cathodic (Electrochemical) Cleaning

This procedure removes adsorbed organics, reduces certain oxides, and prepares the surface for polymer film deposition.

- a) Use a three electrode arrangement in PBKCl (phosphate buffered potassium chloride, pH = 7.2) at RT.
- b) Make the device the working electrode of the 3-E E'Chem cell.
- c) Potentiodynamically cycle over the range –2.0 V to –1.0 V *vs.* SCE. Hydrogen evolution at the cathode and oxygen generation at the anode accompanies cleaning.

- d) Cycle repeatedly until highly reproducible cyclic voltammograms (CVs) are obtained -- typically 5 – 8 min.
- e) Remove and rinse profusely in flowing DI water for 3 min.

III SURFACE ACTIVATION PROCEDURES

A. Activation of Borosilicate Glass

A procedure for producing surface hydroxyls on typical laboratory glass ware (microscope slides, borosilicate or soda lime glass plates, pyrex ware, glass beads, etc.) and silicon oxide surfaces. (CAUTION).

- a) Clean the electrode using an appropriate solvent cleaning procedure (above).
- b) Immerse in 4:1 conc. H_2SO_4 : H_2O_2 (30% aqueous solution) (4:1) (Piranha etch) at 80 °C for 10 s.
- c) Wash in flowing DI water for 3 min.

B. Activation of Platinum

A procedure for producing surface oxide (believed to be a monolayer) with available surface hydroxyls on platinum metal. Such oxide may be subsequently covalently coupled to reactive organosilanes.

- a) Clean electrode using an appropriate solvent cleaning procedure (above).
- b) Electrochemically oxidize in 1.0 M H_2SO_4 at +2.5 V vs. SCE for five (5) min at room temperature.
- c) Wash in flowing DI water for 3 min.

IV RERERENCES

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Anthony Guiseppi-Elie is President and Scientific Director at ABTECH Scientific, Inc., a developer and marketer of chemical and biological sensor devices, instruments, and systems. Anthony holds the Sc.D. in Polymer Materials Science and Engineering from MIT (1983), the M.Sc. in Corrosion Science and Engineering for UMIST, and the B.Sc. in Applied and Analytical Chemistry and Biochemistry from UWI. He completed postdoctoral work at MIT, has studied Business and Technology Management and has been a Visiting Scientist (1995 – '96) in the Department of Biomedical Engineering, Johns Hopkins University School of Medicine.