SILVER MULTI-LAYERS FOR PLANAR Ag/AgCl
REFERENCE ELECTRODES

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ABSTRACT

The behaviour of different multi-layers for silver micro-electrodes is reported. Adhesion, lifetime and the use as a silver/silverchloride reference electrode for biomedical applications has been investigated. The electrodes are incorporated in a planar CMOS-process with a special lift-off technique. The electrodes are used in the development of implantable glucose and oxygen sensors and ion-selective electrodes.

INTRODUCTION

During the last years the research on planar chemical sensors has increased enormously. Since all chemical sensors need a reference electrode, stability and lifetime of this electrode determines the usefulness of the sensor.

For biomedical applications such as dissolved oxygen (Clark-cell) or glucose sensors, usually a Ag/AgCl reference electrode without reference electrolyte is employed. Blood plays in those cases the role of electrolyte.

The potential E at the Ag/AgCl electrode is determined by following equation known as the Nernst equation :

$$E = E^{\circ} - \frac{RT}{nF} \ln [Cl^{-}]$$

where

E° = the standard electrode potential

R = the gas constant

T = the absolute temperature

n = number of electrons participating in the reaction

F = the faraday

$[Cl^{-}]$ = the Cl^{-} -concentration

As in human blood the variations of the Cl^{-} -concentration are very small, the potential at a Ag/AgCl electrode in blood is practically constant. So, in most cases, no internal reference electrolyte is necessary. However, due to the relative high Cl^{-} -concentration, blood is very corrosive. Therefore the corrosion resistance of planar electrodes is of primordial importance.

PROCESSING

A sensor process (ref.1) compatible with a standard 3 μ CMOS process has been developed (fig. 1). The sensor materials are applied after the complete CMOS process. This excludes processing temperatures above 450°C. The process is based on highly doped polycrystalline silicon as interconnection layer between the electrochemical electrodes and the bonding pads. The electrodes are embedded in a silicon dioxide layer, the intermediary oxide between polysilicon and aluminium. This is achieved with a special lift-off technique (ref.2). Lift-off has the inherent advantage that the process is identical for all metals that can be evaporated or sputtered. Patterning of "difficult" metals like Pt, Au or multi-layers is selfevident.

An ideal lift-off profile with overhang is obtained during the wet etching of the silicon dioxide layer (fig. 2). So, etching of contact holes and patterning

of the lift-off mask is done in one step. Each electrode material only needs one extra mask. Adhesion of the electrodes is also improved due to the polysilicon under it. Noble metals like Pt and Au adhere well to polysilicon but do not adhere to silicon dioxide. This has been verified with the Scotch-tape test.

Adhesion of silver to silicon, polysilicon and silicon dioxide however is very poor. Therefore an intermediate film layer as Ti or Cr is used to promote adhesion. These metals corrode easily; mechanical and electrical contact is then lost. So, for Ag/AgCl reference electrodes loss of adhesion is one of the main failure mechanisms. Four different metallisation methods have been investigated : Ag, Cr/Ag, Ti/Ag and Ti/Pd/Ag.

Small electrodes (1.6 mm x 1.1 mm) have been manufactured with the same process as described. All layers are deposited successively with an electron gun evaporation system, (see Table 1). Evaporation is done immediately after the SiO_2 etching. Chemical chloridation of the electrodes is carried out on wafer or on the packaged chip in a $FeCl_3$ (1 %) solution. After encapsulation of the bonding region with a commercial epoxy the respons to a varying Cl^{-} -concentration is measured. Lifetime tests have been carried out on the four different metallisation methods.

MEASUREMENTS

The potential at the different Ag/AgCl electrodes has been measured against a conventional Ingold Ag/AgCl reference electrode with an internal reference electrolyte. The Cl^{-} -concentration in the solution was varied between 10^{-4} M and 1 M. Initially the behaviour is nearly Nernstian for all metallisation methods. A typical respons is shown in fig. 3. However some electrodes started drifting after a few hours; this was related to loss of adhesion of the metal layer. To examine this phenomenon an accelerated lifetime test has been set up.

A significant number of electrodes (24 per metallisation) were immersed in physiological solution at room temperature. Physiological solution simulates blood in its Cl^{-} -concentration and pH (7.4). Every hour the solution was agitated in an ultrasonic way to remove the corroded parts of the metallisation.

With the pure silver electrodes adhesion was lost immediately (fig. 4a). Loss of adhesion of the Ti/Ag was observed after a few hours (fig. 4b). The average lifetime is 2.75 hours. For both metallisation methods the complete electrode lost adhesion. Corrosion of the Cr/Ag electrodes in contrast, started with the formation of blisters and holes. The average time before blister or hole formation is 46 hours (fig. 4c).

The Ti/Pd/Ag electrodes however withstood this lifetime test without any problem. After three months no corrosion or loss of adhesion was observed. On chloridated samples the average lifetime was halved. No damage was found on the chloridated Ti/Pd/Ag electrodes after 3 months. This proves that Ti/Pd/Ag electrodes are far superior to all the other metallisation methods.

An other research group obtained similar results for solar cell metallisations (ref. 3). They related the excellent corrosion resistance to a modification of the anodic potential of the active metal by introduction of palladium, so that a passive oxide is formed when the film is exposed to an electrolyte. Palladium also serves as diffusion barrier for oxygen and moisture. It inhibits the corrosion of the Ti layer and so preserves adhesion of the Ag film.

APPLICATIONS

The Ti/Pd/Ag metallisation has been used with success for different applications. The process described above is now used in the development of implantable glucose and oxygen sensors. For these applications stability and reproducibility of the electrode potential is not critical because the current measurement is carried out at a plateau in the current-potential curve. No problems were encountered with Ti/Pd/Ag/AgCl reference electrodes.

The electrodes were tested as a Clark-cell with Ag cathode and anode (ref.4). The results were positive. Ti/Pd/Ag/AgCl electrodes were deposited on a complete CMOS circuit described in ref.5. For this application, ion-selective sensors, stability and reproducibility is more critical.

CONCLUSION

Planar Ag/AgCl electrodes are incorporated in a standard CMOS process. The corrosion resistance of different multilayers has been investigated. By introduction of palladium as an intermediate layer between titanium and silver, the corrosion resistance increases tremendously without affecting the Nernstian behaviour of the electrode. Immersed in physiological solution, a lifetime of more than three months was observed. The Ti/Pd/Ag/AgCl metallisation has been used with success for different applications.

ACKNOWLEDGMENTS

M. Lambrechts acknowledges support of the IWONL and J. Suls of IMEC, Belgium. We wish to thank J. Vandepuit and V. Muls for processing the devices.

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Fig. 1 Cross-section of a CMOS compatible chemical sensor

Fig. 2 Lift-off profile with overhang

Metal	Thickness [nm]	Evaporation rate [nm/s]
Ti	50	2.5
Cr	50	2.0
Pd	50	1.5
Ag	900	10.0

Table 1

Fig. 3 Cl^- respons of a planar Ag/AgCl electrode (Slope = 57 mV/decade)

Fig. 4.a. Lifetime profile of a Ag layer
(not chloridated)

Fig. 4.b. Lifetime profile of a Ti/Ag layer
(not chloridated)

Fig. 4.c. Lifetime profile of Cr/Ag layer
(not chloridated)