

AN ON-WAFER FABRICATED FREE-CHLORINE SENSOR

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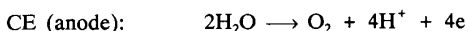
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Abstract

In this paper a method for on-wafer fabrication of free-chlorine sensors is described. The sensor structure consists of a planar three-electrode electrochemical cell covered with a polyHEMA hydrogel membrane. This membrane is photolithographically patterned on-wafer. In order to guarantee a good adhesion of the membrane to the electrode surface a special oxidation consisting of a treatment in an oxygen plasma has been developed followed by a silanization procedure. The optimal operational polarization voltage for detection of free-chlorine was found to be +50 mV vs. SCE. Sensors with membrane thicknesses of 10 and 50 μm were found to give approximately linear calibration curves between 0.1 and 5 mg/l free-chlorine, with sensitivities of 2 and 0.4 nA/(mg/l) respectively.

Introduction

There is an increasing need for the determination and continuous monitoring of residual water disinfectant. A very commonly used chemical for water disinfection is chlorine. Since at pH-values higher than pH 2 free-chlorine is practically exclusively present in the form of hypochloric acid (or its conjugated base) [1], the sensor we present here is based on the electrochemical reduction of mentioned acid. The basic cell consists of a miniaturized, planar electrochemical cell, with a platinum working- and counter electrode, and a partially chlorinated silver reference electrode. The electrode reactions taking place at the working electrode (WE) and counter electrode (CE) are respectively:



Under potentiostatic operation at a properly chosen working potential, the measured current is proportional to the amount of reduced free-chlorine.

When bare electrodes are used in the measurement cell, the mass-transfer to the electrode is strongly influenced by convective effects like stirring. To avoid this, ultra-microelectrodes can be used [2], but then the electrode current decreases. As an alternative, a diffusion limiting membrane (DLM) can be used to define an stagnant surface layer in which diffusion is the only process determining the mass-transfer and thus the measured current. Recently, we have proposed the use of a polyHEMA hydrogel layer as DLM for the detection of hydrogen peroxide [3]. This membrane has the advantage that it can be photolithographically polymerized and patterned enabling the fabrication of the complete cell with IC-compatible methods.

With the technology to deposit polyHEMA membranes, layer thicknesses between 10 and 100 μm can be realized. In this way an optimal trade-off between a high sensor current and a rapid response on one hand (thin membrane) and a stirring insensitive signal on the other hand (thick membrane) can be chosen.

Special attention has to be paid to the adhesion of the polyHEMA membrane. It is known that a chemical pretreatment of oxide surfaces like SiO_2 and Al_2O_3 with a methacrylic functional silane strongly improves the adhesion [4]. However, such a treatment can not be directly applied to the surface of a platinum electrode. Therefore we investigated methods to oxidize and subsequently functionalize a platinum electrode, with the extra requirement that the method should be applicable on-wafer.

Experimental

Basic device fabrication

The basic structure consists of a three-electrode cell realized on a silicon wafer. The working and counter electrodes consist of a 1500 Å thick Pt layer on top of a 500 Å thick Ti adhesion layer. The reference electrode is made by chemical chlorination of a 1 μm thick Ag layer. Further details of the device fabrication are given in [5].

Instrumentation and methods

Cyclic voltammetry measurements were performed using a PAR 273 potentiostat. For all cyclic voltammetric measurements a scan rate of 100 mV/s and an electrolyte of 1 M H_2SO_4 were used, except for the determination of the interference of oxygen reduction relative to the hypochloric acid reduction, where 50 mV/s and 0.1 M KCl with 1% v/v pH 7 buffer (Merck) were used respectively. For chronoamperometric measurements an in-house potentiostat was used, and 0.1 M KCl with 1% v/v pH 7 buffer (Merck) was used as electrolyte. The plasma oxidation of the platinum electrodes was carried out using an oxygen plasma in an Alcatel GIR 300 plasma etch machine. Measurements of polyHEMA membrane thicknesses were carried out with an Alphastep 200 step height profiler. Visual inspection after the measurements confirmed that the scan of the stylus did not cause any damage to the membranes.

Electrode surface modification

Electrochemical oxidation of the platinum electrode surface was carried out by polarizing the electrodes in 1 M H_2SO_4 at + 2.5 V vs. SCE during 5 min. Chemical oxidation was carried out in 0.25 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.5 M HClO, or 1 M HNO_3 . Plasma oxidation was carried out in an oxygen plasma at a frequency of 13.5 MHz, a pressure of 0.1 mbar, and using a power of 100 W.

Silanization of the electrode surface was carried out by dipping the electrodes in hexamethyldisilazane (HMDS) (Fluka). Subsequently, the electrodes were blown dry in nitrogen. Functionalization of the surface with methacrylic groups was carried out by treating the electrodes for 1 minute with a solution of 10% (trimethoxysilyl)propyl methacrylate (TMSM) (Aldrich) and 0.5% H₂O in toluene at 60 °C.

Membrane deposition

The monomer mixture consisting of 57.5% wt. hydroxyethyl methacrylate (HEMA) (Fluka), 38% wt. ethyleneglycol (EG) (Merck), 1% wt. dimethoxyphenylacetophenone (DMPAP) (Aldrich), 2.5% wt. polyvinylpyrrolidone K90 (PVP) (Aldrich) and 1% wt. tetraethyleneglycol dimethacrylate (TEGDM) (Fluka) was placed by pipette on the wafer in an amount corresponding to the required membrane thickness. A Mylar sheet was then pressed onto the mixture which was allowed to spread out over the wafer until the required coverage of the wafer was obtained. Then the monomer mixture was selectively photopolymerized using a photomask with UV-light. Exposition times of 30 s. to 3 min. were used. This was followed by development in ethanol. The sensors were preconditioned in 0.1 M KCl prior to measurement.

Results and discussion

Surface modification of the electrodes

In the fabrication process of the completed cell with hydrogel membrane, a crucial element concerning the durability is the membrane adhesion to the electrode surface. In order to be able to apply the frequently used method of surface silanization, the surface of the platinum electrodes has first to be oxidized. A well-known standard method to do this is electrochemical oxidation [6]. The formation of oxide (mono)layers at the electrode surface can be monitored by reducing the oxide in a cathodic scan starting at high anodic potential. In figure 1 stripping voltammograms of platinum, untreated and electrochemically oxidized for respectively 1 s., 3 min. and 5 min. are shown. From this figure, a clear

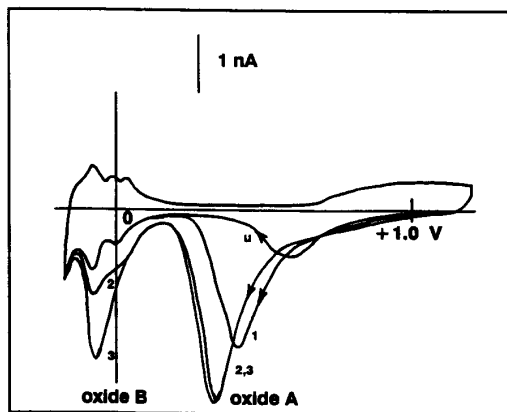


Figure 1. Cathodic stripping voltammograms of bare Pt-electrodes in 1 M H₂SO₄ after anodic polarization at +2.5 V vs. SCE. u: untreated 1: 1 s., 2: 3 min., 3: 5 min.

distinction between the two different cathodic waves can be distinguished: one that is quickly formed, and easily reduced (reduction potential +350-450 mV/SCE), and a second wave that is only formed after a few minutes polarization at +2.5 V/SCE, and reduced at approximately -50 mV/SCE. The presence of these two waves is in good correspondence with the results reported in [6], where they were attributed to two different forms of platinum oxide. We will also designate the two waves as A and B for the more anodic and more cathodic wave respectively, in accordance with the nomenclature used in [6].

In order to see which one of the two oxides is necessary for the silanization, we performed a simple silanization reaction with HMDS which is comparable to the somewhat more elaborate reaction with TMSM. Such a reaction should passivate the formed oxide, and disable its electrochemical reduction. In figure 2 the effects of the silanization on the appearance of both oxide peaks is shown. From the three curves representing untreated oxide, oxide treated in HMDS for 30 s., and oxide treated in HMDS for 5 min., two conclusions can be drawn. The first and most important conclusion is that the oxide represented by wave A does not react with HMDS. The second conclusion is that wave B reacts only relatively slowly with HMDS, and that it takes about 5 min. to obtain a fully passivated oxide.

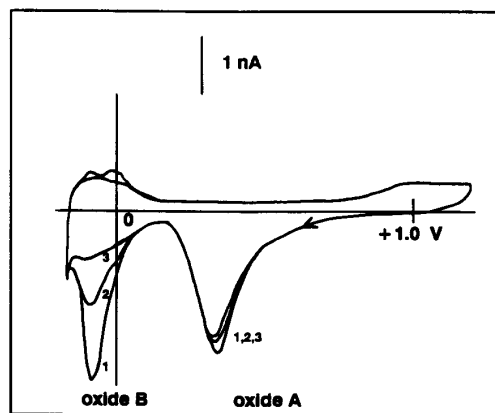


Figure 2. Cathodic stripping voltammograms of Pt-electrodes, electrochemically oxidized during 5 min. in 1 M H₂SO₄ and treated with HMDS. 1: no HMDS treatment, 2: 30 s. HMDS, 3: 5 min. HMDS.

From the above results it can be concluded that in order to be able to silanize the electrode surface, the formation of platinum oxide of type B is necessary. Since electrochemical oxidation is not easily applicable on whole wafers, we investigated other chemical treatments that could provide the platinum oxide type B. Unfortunately, treatments with oxidants like nitric acid, hypochloric acid, and ammoniumperoxodisulfate did not result in the appearance of the oxide type B. The only treatment which did give both oxide waves was a treatment in oxygen plasma, as shown in figure 3. From this figure it can be concluded that a 5 min. treatment of the platinum electrode in an oxygen plasma results in similar A- and B-type oxygen waves as obtained with the electrochemical oxidation.

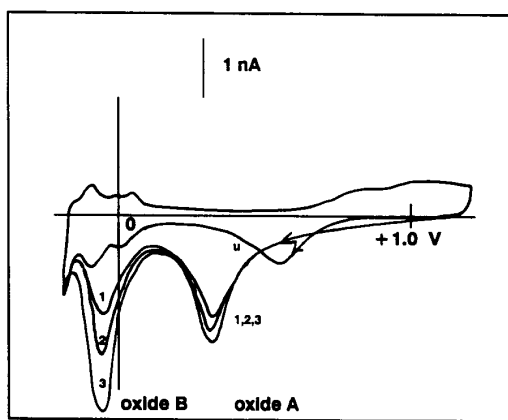


Figure 3. Cathodic stripping voltammograms of bare Pt-electrodes in 1 M H_2SO_4 after treatment in oxygen plasma. u: untreated, 1: 30 s., 2: 2 min., 3: 5 min.

Membrane deposition

The deposition of the polyHEMA hydrogel membranes was carried out as described in the experimental part. Some difficulties were encountered when we tried to wash away the unpolymerized regions from the wafer in the development step. Therefore we had to modify the mask in such a way that only every second basic electrode was covered with the polyHEMA membrane. A SEM micrograph of a part of a wafer covered with membranes is shown in figure 4. From this figure, it can be concluded that a satisfactory lateral resolution of some tens of microns is

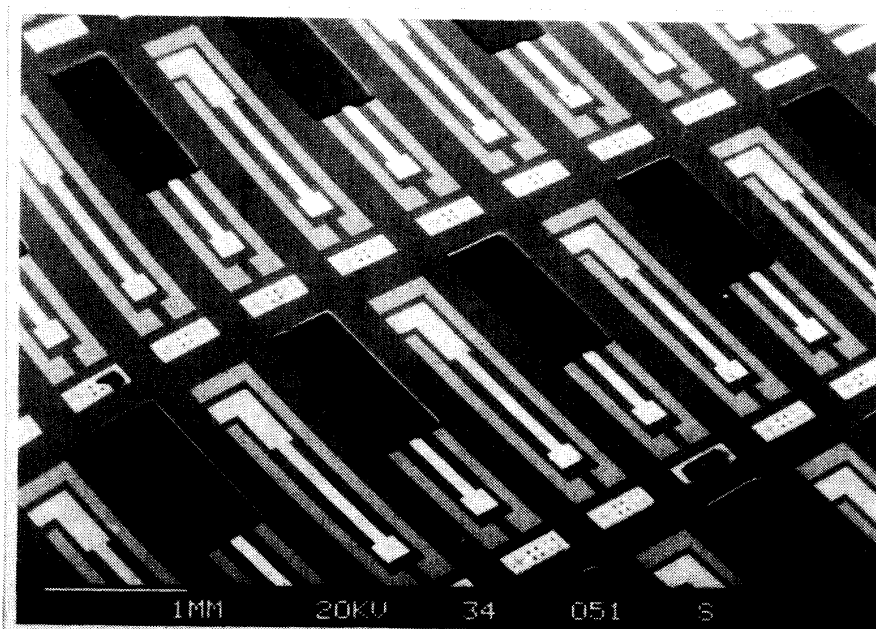


Figure 4. SEM micrograph of part of a wafer with a photopolymerized hydrogel membrane on every second device.

obtained, which is largely sufficient for our purpose.

The homogeneity of the membrane thickness over the wafer was investigated by step-height measurements. On 32 evenly distributed membranes over the wafer a mean thickness of $61.8 \mu m$ was found with a standard deviation of $7.3 \mu m$. An important part of the thickness variation was caused by a continuous varying thickness of the membranes over the wafer. If closely located membranes were considered, typical standard deviations of $3-4 \mu m$ were found.

Sensor characterization

A first characterization of the electrodes was carried out to determine the optimal polarization potential for the detection of free-chlorine. Therefore, cyclic voltammograms were taken of the bare platinum electrodes in background electrolyte under nitrogen and with added hypochloric acid. In order to examine the interference of oxygen, a third cyclic voltammogram was recorded in background electrolyte and ambient air. The results are shown in figure 5. For the reduction of hypochloric acid a very sluggish wave is found at $-200 mV$ vs. SCE, with a broad slope at more positive potentials indicating a non-reversible behavior. The cyclic voltammogram taken in ambient air indicates a strong oxygen interference, starting at potentials lower than $0 mV$ vs. SCE. It has to be remarked here that the finally desired detection limit for free-chlorine is in the micromolar range, whereas the figure shown is obtained with 1 millimolar free chlorine.

The above mentioned conclusions were verified with potentiostatic measurements carried out with mounted and encapsulated three-electrode cells covered with a polyHEMA membrane of approximately $10 \mu m$ thickness. In figure 6, the sensor current as a function of the free-chlorine concentration at different polarization potentials is measured. Clearly, at the most cathodic potential ($-50 mV$

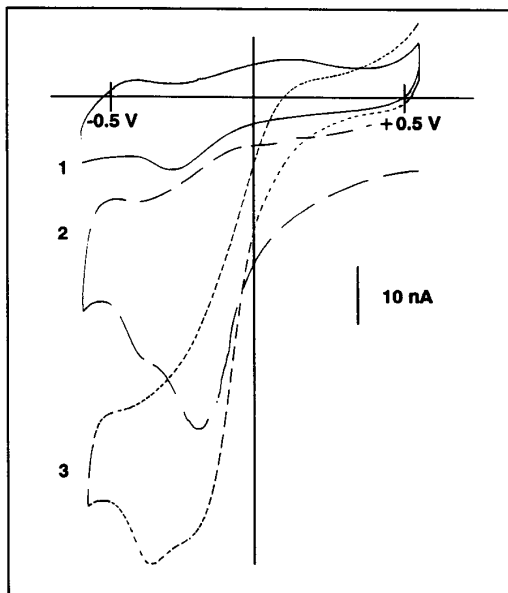


Figure 5. Cyclic voltammograms of platinum electrodes in 0.1 M KCl, pH 7. 1: under N_2 , 2: with $10^{-3}M$ HClO, 3: as 1, in ambient air.

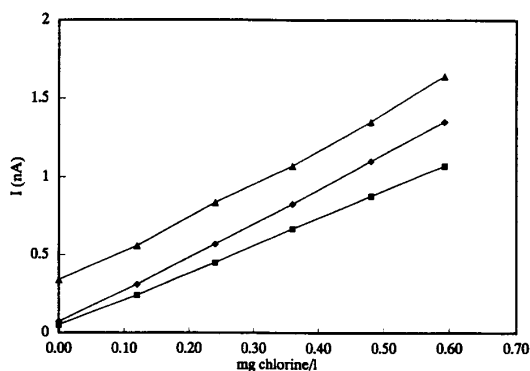


Figure 6. Sensitivity curves of completed sensors with an approximately $10 \mu m$ thick polyHEMA membrane. Polarization potentials: upper curve: $-50 mV$ vs. SCE, middle curve: $+50 mV$ vs. SCE, lower curve: $+150 mV$ vs. SCE.

vs. SCE) an offset current due to the reduction of oxygen is found. At $+50 mV$ vs. SCE this offset current is largely suppressed, whereas the same sensitivity to free-chlorine is maintained. A further increase of the polarization potential results in no further decrease of the offset current, while the sensitivity starts to decrease. Therefore, it was concluded that $+50 mV$ vs. SCE is the optimal polarization potential.

Finally, a calibration graph of two completed sensors was taken membranes of thickness 10 and $50 \mu m$. The results are shown in figure 7. A slight difference in the sensitivity is observed for both sensors between low and high free chlorine concentrations: 2.2 respectively $1.8 nA/(mg/l)$ for $10 \mu m$ polyHEMA, 0.45 respectively $0.3 nA/(mg/l)$ for $50 \mu m$ polyHEMA. The approximate sensitivity ratio of 5.5 ± 0.5 closely reflects the thickness ratio of the membranes.

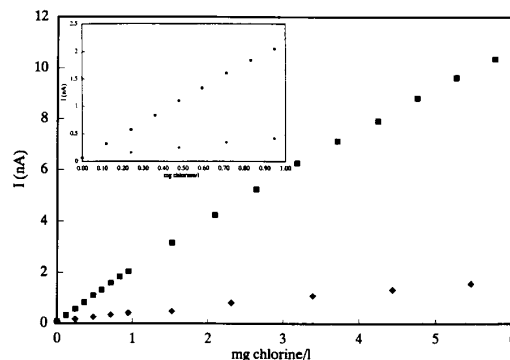


Figure 7. Calibration curve of two sensors with respectively $10 \mu m$ (upper curve) and $50 \mu m$ (lower curve) thick polyHEMA membranes. Polarization potential: $+50 mV$ vs. SCE. The inset shows the low concentration part of the curve in more detail.

Conclusions

It has been shown that with the method presented membrane-covered electrochemical cells can be realized on-wafer. A special oxidation was found to be necessary for the platinum electrodes to be able to carry out the surface silanization, since the standard electrochemical oxidation is not easily performed on whole wafers. Using cathodic stripping voltammetry, it was found that oxidation in oxygen plasma resulted in the same oxidized surface state of the platinum electrode as with the electrochemical oxidation.

Both cyclic voltammetric measurements using bare electrodes as well as chronoamperometric measurements with hydrogel covered electrodes resulted in $+50 mV$ vs. SCE as the optimal polarization potential. The calibration curves obtained with sensors having two different membrane thicknesses using this polarization potential revealed a nearly linear sensor response over the range from 0.1 to $5 mg/l$ free-chlorine.

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