On-wafer fabricated free-chlorine sensor with ppb detection limit for drinking-water monitoring

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Abstract

The fabrication and characterization of a planar silicon-based sensor for free chlorine, present in the form of hypochlorous acid, is presented. The sensor uses a three-electrode electrochemical cell, with thin-film platinum working and counter electrodes, and a thin-film partially chloridized silver reference electrode. The working electrode is covered with a photopolymerized polyHEMA hydrogel membrane, which serves as a diffusion-limiting membrane. All electrodes are contacted by polysilicon films isolated with silicon nitride, to obtain a precise definition of the electrode area and to make the encapsulation less critical. The optimal polarization potential for hypochlorous acid detection at which there is no interference from the reduction of dissolved oxygen is +350 mV versus SCE. Calibration curves show an excellent linearity ($R^2 = 0.9996$, $n = 21$) and a sensitivity of approximately 10 nA/(mg chlorine/l). The detection limit ($S/N = 3$) is approximately 1 μg chlorine/l (1 ppb).

1. Introduction

The early detection of organic pollutants in drinking water is of essential importance for the quality control of drinking water. The depletion of residual disinfectant used to eliminate these pollutants is an indication for the presence of organic pollution, which makes the continuous monitoring of disinfectant residual of great interest. The most commonly used chemical for water disinfection is chlorine, present in the water as hypochlorous acid or, at pH values above 7.5, as the hypochlorite anion. The levels of the free chlorine to be detected are typically between 0 and 0.1 mg/l, which means that the detection limit and sensitivity of the sensor are very important. Since free chlorine has its highest disinfecting reactivity when present as hypochlorous acid [1, 2], a sensor for this form has been developed. Amperometric detection has been chosen as the measurement principle, because hypochlorous acid can easily be reduced electrochemically due to its strong oxidative nature.

The basis of the sensor is a three-electrode planar electrochemical cell covered by a hydrogel-type diffusion-limiting membrane. Earlier [3] we presented the use of an on-wafer deposition and patterning technique to realize these membranes. However, the surface area of the working electrode used in that study was small, and it appeared difficult to obtain a durable adhesion between the hydrogel membrane and the epoxy used for encapsulation. For both problems, a solution will be presented by using another technology for the fabrication of the transducer.

2. Technology and basic device fabrication

As mentioned before, the thin films of platinum used in an earlier design served at the same time as electrode and as bonding pad [3, 4]. Thus, the finally obtained electrode area was defined by the precision of the encapsulation and was thus difficult to control. Therefore, for the new design of the basic device, 1500 Å thick phosphorus-doped polysilicon contacts, isolated with a 2000 Å thick silicon nitride layer, were used to connect the three electrodes to their respective bond-wire contacts. Platinum working and counter electrodes were deposited by lift-off on the polysilicon with the use of a 50 Å intermediate Ti adhesion layer. The electrical contacts Pt/n-polySi/Pt were verified to be ohmic. A 1 μm thick Ag film was deposited as reference electrode. In addition, compared to the earlier presented design, the electrode area was increased by a factor of 15 to 1.5 mm^2. A photograph of the silicon-based three-electrode device is shown in Fig. 1.

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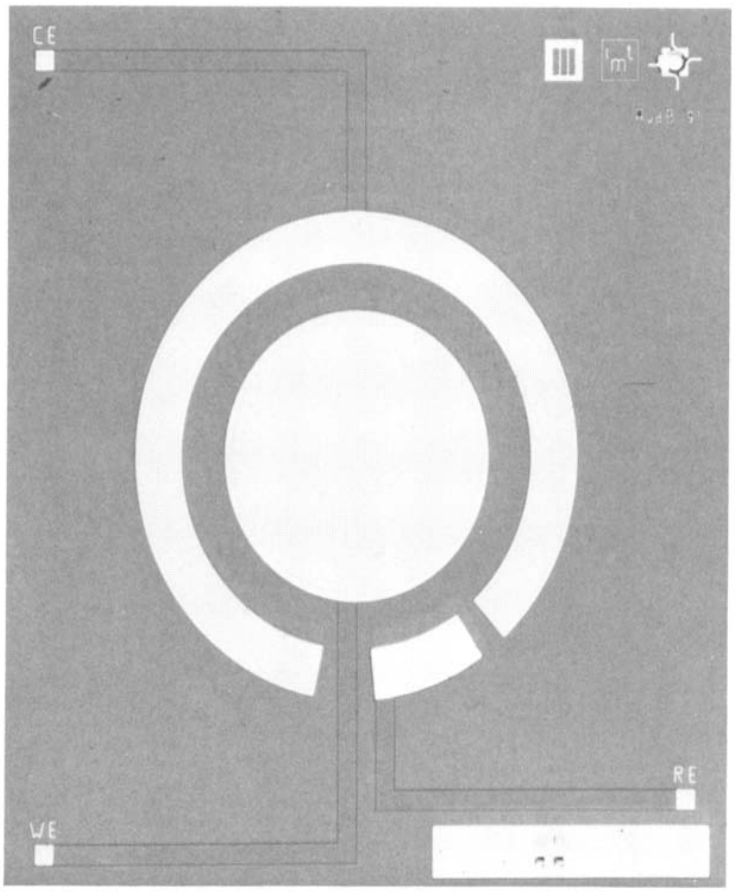


Fig. 1. Photograph of the transducer with platinum working (centre) and counter (ring) electrodes and silver reference electrode (ring-segment) contacted by polysilicon.

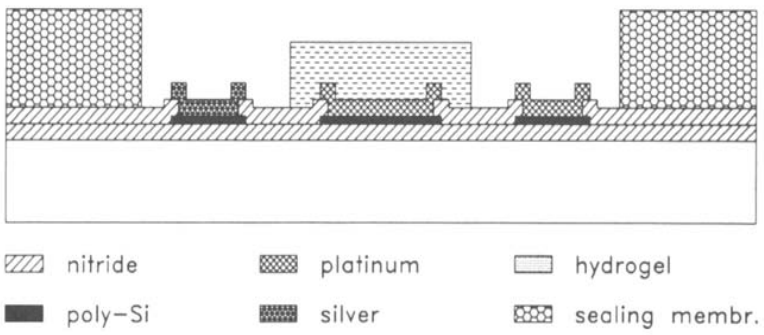


Fig. 2. Cross section of the free-chlorine sensor with electrodes and polymeric membranes.

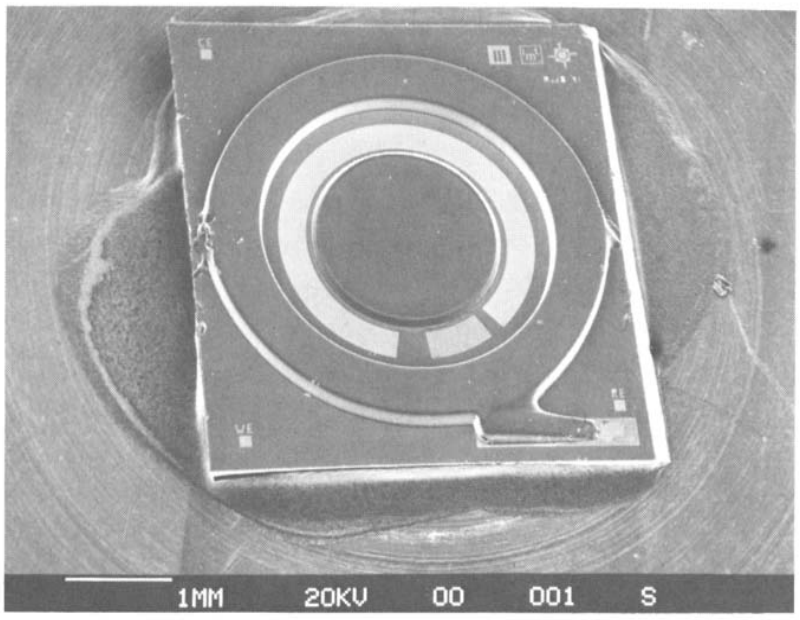


Fig. 3. SEM micrograph of a completed free-chlorine sensor chip.

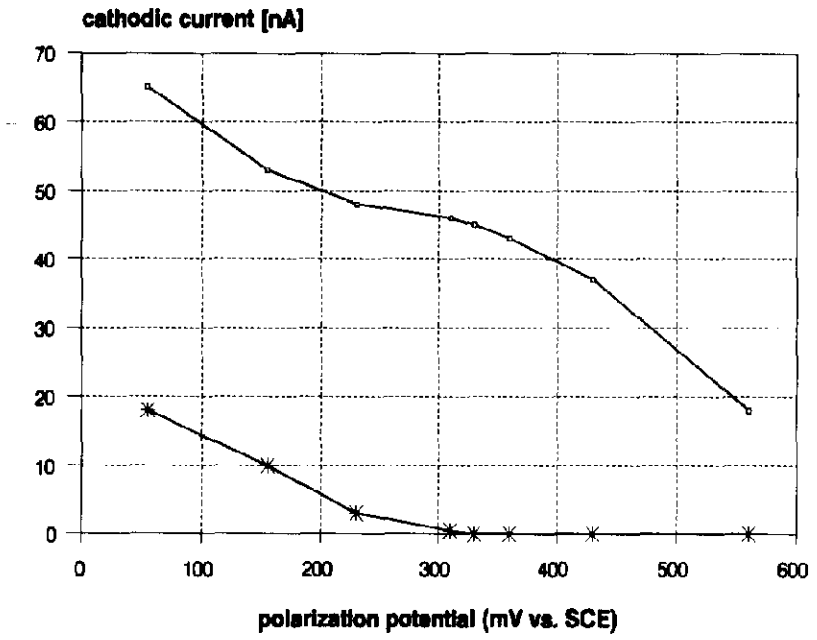


Fig. 4. Cathodic sensor current as a function of polarization potential in phosphate buffer pH 5.5 without chlorine (lower curve) and with 4 mg chlorine/l (upper curve).

3. Sensor characterization

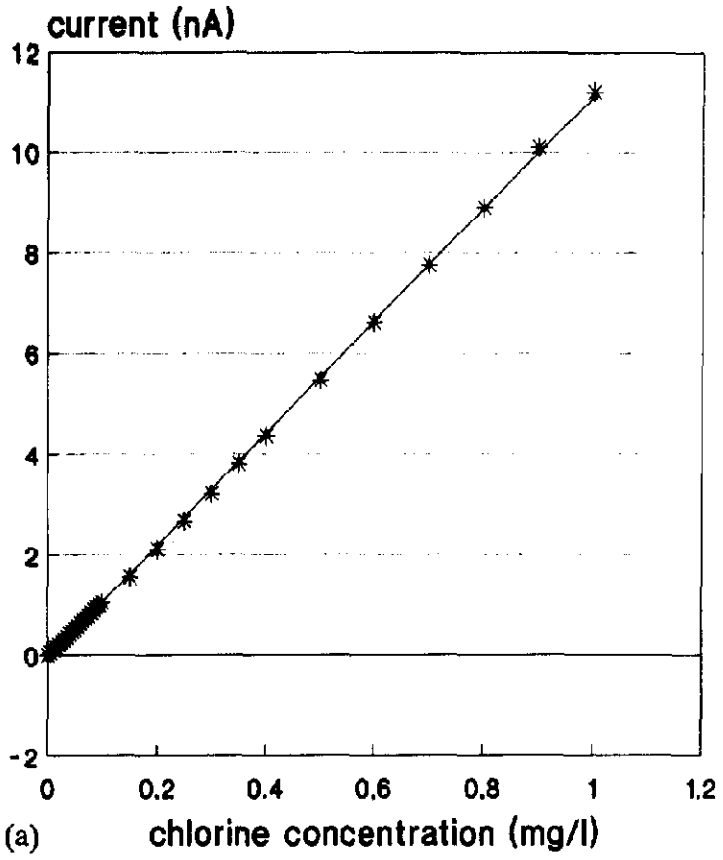
The working electrode is covered by a photolithographically patterned polyHEMA hydrogel membrane, chemically anchored to the platinum electrode and the surrounding Si_3N_4 with the help of a chemical pretreatment consisting of a plasma oxidation followed by a silanization [5, 6]. A second photopolymerized polysiloxane membrane is added to the structure in order to provide a hermetic ring for encapsulation on the one hand, and to incorporate the sensor in an easy way in a flow-through set-up, on the other hand. The reference electrode, a partially chloridized silver film, can be used in drinking water since the concentration of chloride ions is fairly constant. A cross section of the structure is shown in Fig. 2, whereas in Fig. 3 an SEM micrograph of a complete device with hydrogel diffusion membrane and encapsulation ring is shown.

Before measuring the chlorine sensitivity of the sensor, the optimal polarization potential for hypochlorous acid reduction was determined. In Fig. 4 the cathodic sensor current as a function of polarization potential is shown in a background phosphate buffer (pH 5.5) with and without 4 mg/l chlorine. As is shown in the Figure, at potentials more cathodic than 325 mV versus SCE, the oxygen reduction starts (lower curve). On the other hand, from the upper curve a current plateau can be observed between 250 and 350 mV, thus 350 mV versus SCE was determined as the optimal working potential

The sensor sensitivity to hypochlorous acid was investigated by addition of a diluted NaClO standard solution (calibrated by the DPD method) to a 3×10^{-4} M NaCl, 10^{-4} M phosphate buffer solution adjusted to pH 5. A miniature potentiostat (BAsys Sensor Instrumentation) was used to polarize the working elec-

trode at +175 mV versus the on-chip Ag/AgCl reference electrode (+350 mV versus SCE). The results, shown in Fig. 5(a) and (b), show a very good linear response over the range 0–1 mg/l chlorine (linear regression: $r^2 = 0.9996$, $n = 21$). A variation of approximately ±10% was found in the sensitivity of different sensors, which may be mainly attributed to variations in the thickness of the hydrogel membrane.

For the sensor's detection limit, a measurement set-up in a Faraday cage was used in order to avoid as much as possible electronic noise, easily picked up at the current levels involved. In addition, to avoid effects of trace chlorine consumption by the polymer used to encapsulate the sensor chip, the measurements were carried out in a flow-through set-up. Finally, an electronic low-pass filter (0.2 Hz) was used to suppress noise. The result, as shown in Fig. 6, indicates that the detection limit is approximately 1 ppb, with a signal to noise ratio of three. The response time is around 30 s for rising concentrations, whereas it takes the sensor about 3 min to restabilize at its baseline.



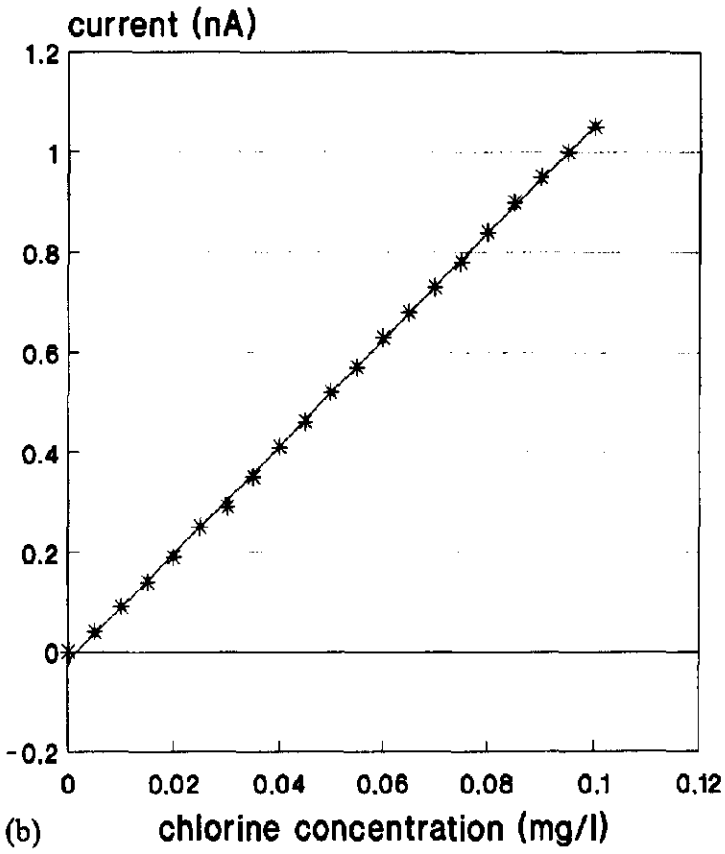


Fig. 5. Sensor output current as a function of hypochlorous acid concentration: (a) high concentration range; (b) low concentration range.

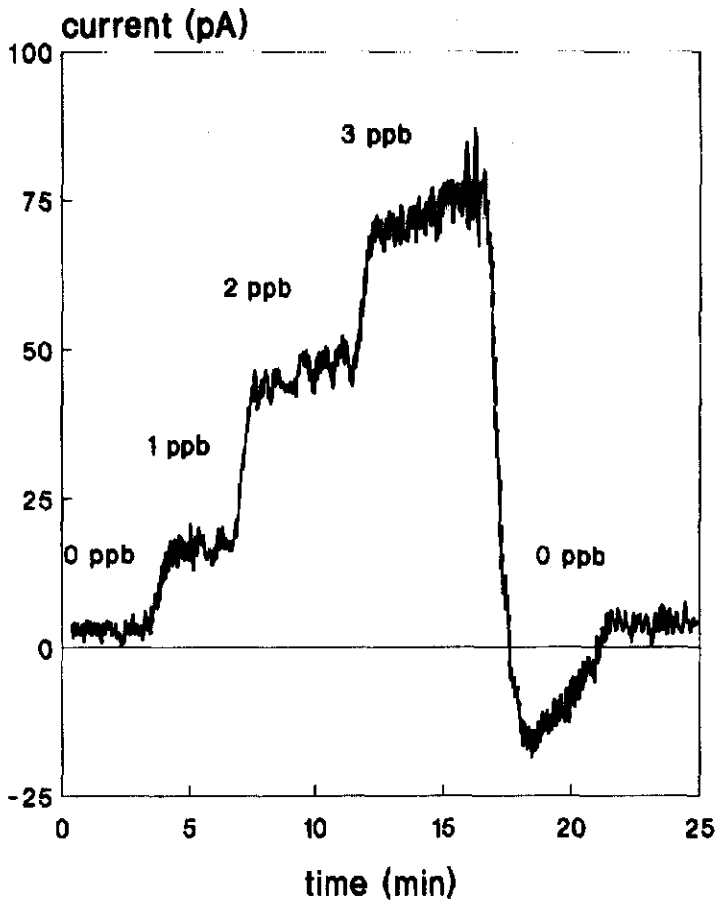


Fig. 6. Sensor response to very small additions of hypochlorous acid showing the sensor's detection limit.

Finally, two previously calibrated sensors were tested under real conditions on-site in a water-treatment plant. The operating conditions were a pressure of approximately 3 bar, and a flow velocity of 1–2 m/s. The results were compared with a conventional HACH analyser and showed good agreement. A critical element of the sensor is the lifetime of the Ag/AgCl reference electrode, which tends to dissolve slowly in the continuous water flow.

4. Conclusions

We have shown that a sensor for free chlorine can be fabricated with IC-compatible techniques. At a properly chosen potential (+350 mV versus SCE), the sensor shows a good sensitivity to free chlorine, while there is no interference from dissolved oxygen. With the use of polysilicon contacts, we have been able to obtain a well-defined working electrode area, which, by its size, provides a sufficiently high reduction current to be

measured without difficulty. The sensor has a very good linear response in the range of interest, and a detection limit of 1 ppb. Finally, the correspondence with a commercial analyser indicates that the application of the sensor under real circumstances looks very promising. Future research will focus on the increase of the reference electrode lifetime.

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References

1 V. L. Snoeyink and D. Jenkins, *Water Chemistry*, Wiley, New York, 1980, p. 388.

2 G. C. White, in *The Handbook of Chlorination*, Van Nostrand Reinhold, New York, 1986, p. 256.

3 A. van den Berg, A. Grisel, M. Koudelka and B. H. van der Schoot, A universal on-wafer fabrication technique for diffusion-limiting membranes for use in micromechanical amperometric sensors, *Sensors and Actuators B, 5* (1991) 71.

4 S. Gernet, M. Koudelka and N. F. de Rooij, Fabrication and characterization of a planar electrochemical cell and its application to a glucose sensor, *Sensors and Actuators, 18* (1989) 59.

5 A. van den Berg, M. Koudelka-Hep, B. H. van der Schoot, E. Verney-Norberg, A Grisel and N. F. de Rooij, Silicon-based chlorine sensor with on-wafer deposited chemically anchored diffusion membrane. Part I. Basic sensor concept, *Anal. Chim. Acta, 269* (1992) 75–82.

6 E. J. R. Sudhölter, P. D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld and D. N. Reinhoudt, Modification of ISFETs by covalent anchoring of poly(hydroxyethyl methacrylate) hydrogel. Introduction of a thermodynamically defined semiconductor–sensing membrane interface, *Anal. Chim. Acta, 230* (1990) 59–65.