

Strategies of Miniaturised Reference Electrodes Integrated in a Silicon Based “one chip” pH Sensor

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Abstract: Different types of Ag/AgCl reference electrodes have been realised by means of thin- and thick-film technique. For inner electrolyte, KCl-containing membranes have been deposited and different coatings have been used to protect the reference electrode from a fast leaching out of KCl. The stability of the potential of the reference electrodes **without** KCl-containing membranes in 3 M KCl was about 7 hours for thin-film electrodes and up to 90 hours for thick-film electrodes. The reference electrodes **with** membrane were stable for more than two months. The thick-film reference electrode was integrated with a thin-film pH sensor onto one chip and the system pH sensor/reference electrode was investigated by means of capacitance/voltage (C/V) and constant capacitance (ConCap) mode.

Keywords: reference electrode, thin-film technique, thick-film technique, “one chip” sensor, pH sensor.

Introduction

The development of miniaturised electrochemical sensors have increased dramatically during the last twenty years [1,2]. The established silicon technology offers the possibility to create a variety of potentiometric sensors for the detection of (bio-)chemical analytes in aqueous solutions. However, one of the serious problems that has restricted their early commercialisation is the missing miniaturised reference electrode, which is an essential component, e.g. in potentiometric measurements. As for the

conventional reference electrode, such a miniaturised reference electrode must possess a stable potential that is invariant with solution composition. Although the composition of a conventional macroscopic reference electrode with inner electrolyte and diaphragm is not easy to transfer in a silicon-based miniaturised system, within the last years, some attempts have been made to realise miniaturised reference electrodes using thin- and thick-film techniques [3-8]. Nevertheless, no miniaturised reference electrode has been fabricated so far that has nearly identical features like conventional ones.

In this paper, we describe the design, fabrication and electrochemical characterisation of miniaturised thin- and thick-film Ag/AgCl reference electrodes. To increase the potential stability and to decrease the cross-sensitivity towards chloride ions, KCl-containing agar agar membranes and different protective coatings have been used. The realised reference electrode has been integrated with a thin-film pH sensor, that has a capacitive EIS (Electrolyte-Insulator-Semiconductor) structure together on one chip, for the first time.

Experimental

Three different technologies have been used to fabricate the Ag/AgCl layer of the miniaturised reference electrodes:

- evaporation of Ag and further chlorination of the Ag to AgCl (type 1: Ag/AgCl),
- evaporation of Ag and deposition of Ag₂S (65%)/AgCl (35%) by means of pulsed laser deposition (PLD) (type 2: Ag/PLD),
- deposition of Ag/AgCl ink by means of thick-film technique (type 3: SPE (screen-printed electrodes)).

For the fabrication of the thin-film reference electrodes of type 1, a 500 nm thick SiO₂ layer was thermally grown in wet air (oxidation oven, Fa. Tempress) on top of the p-doped <100> silicon wafer (Fa. Wacker-Chemitronic). Then, the wafer was structured by means of photolithographic processes and a layer composition of Ti (10 nm)/Pt (50 nm)/Ag was deposited by means of electron beam evaporation (L 560, Fa. Leybold AG). The thickness of the Ag layer was 300 nm, 1 μm or 3 μm, respectively. After separation into single chips of 1 cm * 2 cm, the Ag surface was chlorinated to AgCl. The chlorination process was performed in a solution of KCl/AgNO₃ (1 M, pH 1) at a constant current of 0.2 mA. To study an influence of the layer thickness on the characteristics of the reference electrode, AgCl layers with different thicknesses have been prepared by chosen different chlorination times between 1 and 60 minutes.

For the realisation of the thin-film reference electrodes of type 2, after oxidation and structuring of the silicon wafer, a layer composition of Ti (10 nm)/Pt (50 nm)/Ag (300 nm) was deposited by means of electron-beam evaporation. After separation into single chips, a Ag₂S (65%)/AgCl (35%) compound was deposited by means of pulsed laser deposition (PLD). The deposition times were 10 minutes, 20 minutes or 40 minutes, respectively.

The thick-film reference electrodes (type 3) were fabricated with conventional screen-printing technique. Therefore, a Ag/AgCl ink (Ercon R-414) was printed through a patterned stencil (Fa. Jotek)

on an oxidised silicon wafer. The resulting printed thick-film reference electrodes were cured for 2 hours at 120°C and then, the wafer was separated into single chips.

All types of reference electrodes were bonded on a printed circuit board and contacted on the Ag/AgCl strip. Finally, they were encapsulated with an epoxy compound (Scandiplast, Fa. Tempelmann) in that way, that only a circle of a diameter of 0.38 cm² was opened.

In contrast to the conventional reference electrodes with an inner electrolyte, for miniaturised reference electrodes a KCl-containing agar agar membrane was used. Therefore, 0.5 g of agar agar powder (28,289-8, Fa. Aldrich) was soluted in a 0.5 M AgCl/KCl solution and heated at a temperature of about 150°C for two hours. About 0.5 ml of membrane solution was dropped in an open area, zoned by an o-ring seal. After some minutes the solution gets gelic. To protect the agar agar membrane from a fast leaching out of the chloride ions, the membrane was covered with a polyvinylchloride/cellulose nitrate layer (PVC/CN) or a polyvinylchloride/nafion layer (PVC/N). To realise the PVC membrane, 50 weight % PVC powder (81392, Fa. Fluka), KCl and 50 weight % 2-nitrophenyl-octylether (NPOE, 73732, Fa. Fluka) were soluted in THF (87369, Fa. Fluka) and after stirring, a thin layer has been deposited on the surface of the agar agar membrane (amount about 30 µl). As an additional protective coating, a cellulose nitrate (N7892, Fa. Sigma) or nafion 117 (27,467-4, Fa. Aldrich) membrane was deposited onto the PVC layer and fixed with silicone. In Fig. 1, a cross section of reference electrodes with KCl-containing membrane and protective layer is demonstrated.

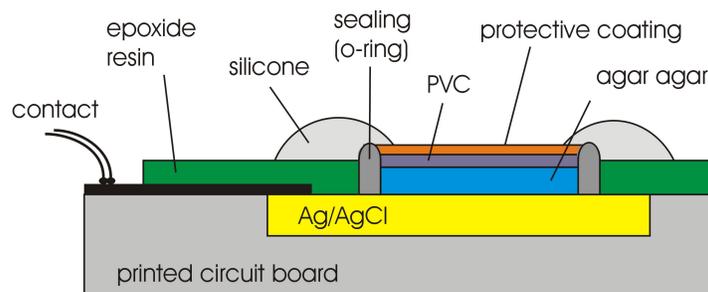


Figure 1. Cross section of the miniaturised reference electrodes with KCl-containing membrane and protective coating.

Three different types of reference electrodes **without** KCl-containing membrane have been characterised in terms of potential stability in 3 M KCl solution. The potential was recorded versus a conventional Ag/AgCl reference electrode with 3 M KCl as inner electrolyte. The electrochemical investigation in terms of potential stability and cross-sensitivity of the reference electrodes **with** KCl-containing membrane has been performed in Titrisol buffer, pH 7. The potential of the miniaturised reference electrodes were measured versus a conventional double-junction reference electrode with 3 M KCl as inner electrolyte and 0.1 M KNO₃ as outer electrolyte. The cross-sensitivity of the reference electrodes **with** membrane towards chloride ions was detected in Titrisol buffer, pH 7, in the concentration range between 10⁻⁴ M KCl and 10⁻¹ M KCl.

To investigate the possibility of integration of miniaturised reference electrodes in a potentiometric sensor system, a thick-film reference electrode without membrane was combined with a thin-film pH sensor onto one chip. A cross section of a thin-film pH sensor with integrated thick-film reference electrode is shown in Fig. 2. In a first step the capacitive Si/SiO₂/Si₃N₄ structure of the pH sensor was

fabricated. The fabrication of the thin-film pH sensor with an EIS (Electrolyte-Insulator-Semiconductor) structure is described in detail elsewhere [9-12]. To avoid the influence of a parasitic capacitance, the Ag/AgCl ink has been deposited on an approximately 1.5 μm thick SiO_2 layer, fabricated by means of PECVD (plasma-enhanced chemical vapor deposition). The “one chip” sensor (pH sensor/reference electrode) was characterised by means of capacitance/voltage (C/V) and constant capacitance (ConCap) methods in the concentration range between pH 5 and pH 7 (Titrisol buffer). The concentration of the chloride ions was kept constant to about 0.05 mM.

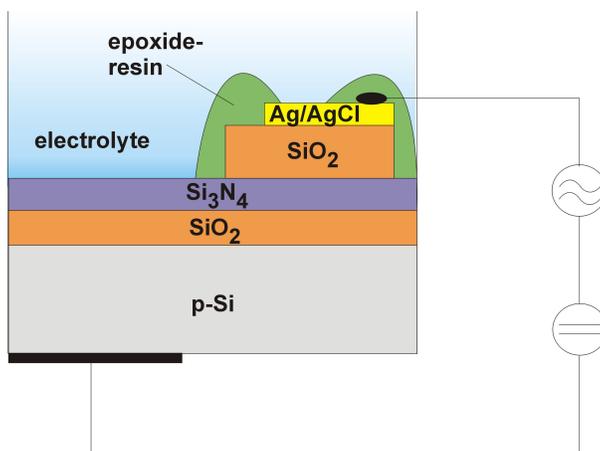


Figure 2. Cross section of the pH sensor (thin-film) with miniaturised reference electrode (thick-film) together on one silicon chip.

Results and Discussion

The stability of the potential of the miniaturised reference electrodes **without** membrane was investigated for four days in a 3 M KCl solution. Because the potential is measured versus a conventional reference electrode with also 3 M KCl as inner electrolyte, it should be nearly zero. For all electrodes this has been observed immediately after starting the measurement. The stability of the reference electrodes, fabricated by means of evaporation/chlorination (type 1), was dependent on the chlorination time (i.e., on the thickness of AgCl) but independent on the original thickness of Ag. For this type of electrode, the maximum stability has been observed for the reference electrodes prepared by a 60 minute chlorination of a 3 μm thick Ag layer. The so produced reference electrodes were stable for about 7 hours. The stability of reference electrodes, fabricated by means of PLD process (type 2), were nearly independent on the thickness of the $\text{Ag}_2\text{S}/\text{AgCl}$ layer. This type of electrode has the shortest time of a stable potential (about 0.5 hours), whereas the thick-film reference electrodes (type 3) were stable for up to 90 hours, also dependent on the thickness of the Ag/AgCl layer. The stability of these three types of reference electrodes are compared in Fig. 3, where the potential of the electrode is plotted versus the time in solution.

Thus, the investigations of different types of reference electrodes **without** KCl-containing membrane have shown that those electrodes, fabricated by means of evaporation/PLD (Ag/PLD) were less stable in 3 M KCl than the other electrode types. Therefore, only the reference electrodes of type 1

and type 3 were covered with a KCl-containing agar agar membrane and a protective coating of PVC/cellulose nitrate (CN) or PVC/nafion (N). The stability of these electrodes have been investigated over the time period of more than two months. During this time, the electrode potential was periodically checked for a measurement time of about 10 hours. To evaluate the stability of the respective reference electrode types during the measurement period of two months, the maximum difference of the start potential during this time was calculated for each electrode. This is plotted in Fig. 4 for the different electrode types and protective coatings. The reference electrodes, fabricated by

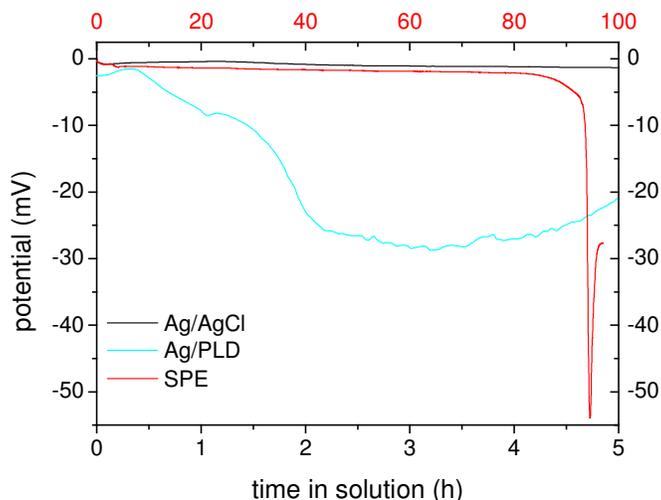


Figure 3. Potential stability of different miniaturised reference electrodes **without** KCl-containing membrane measured versus a conventional reference electrode.

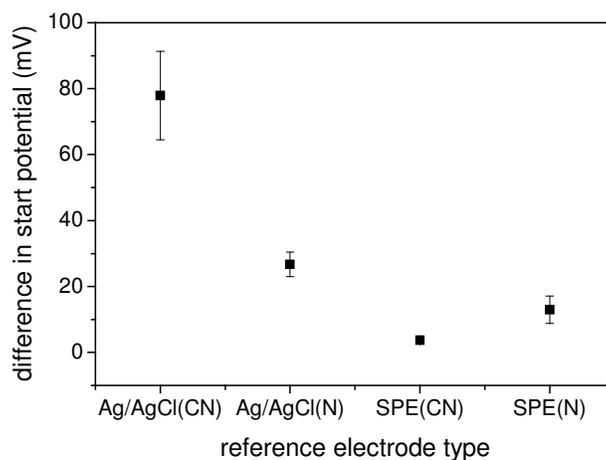


Figure 4. Difference in start potential of different miniaturised reference electrodes **with** KCl-containing membrane and protective coating.

means of evaporation/chlorination (type 1) have a variation of the start potential of more than 19 mV. In contrast, the screen-printed electrodes (type 3) possess smaller variations of the start potential. The smallest change in the start potential, however, was found for the type 3 electrodes with PVC/CN as protective coating (less than 4 mV), whereas the type 3 electrodes with PVC/N coating have a variation of about 13 mV.

Fig. 5 shows the averaged drift rate for the same reference electrodes. Therefore, the difference of the potential at the beginning and the end of each 10 hour measurement was calculated and divided by the measurement time of 10 hours.

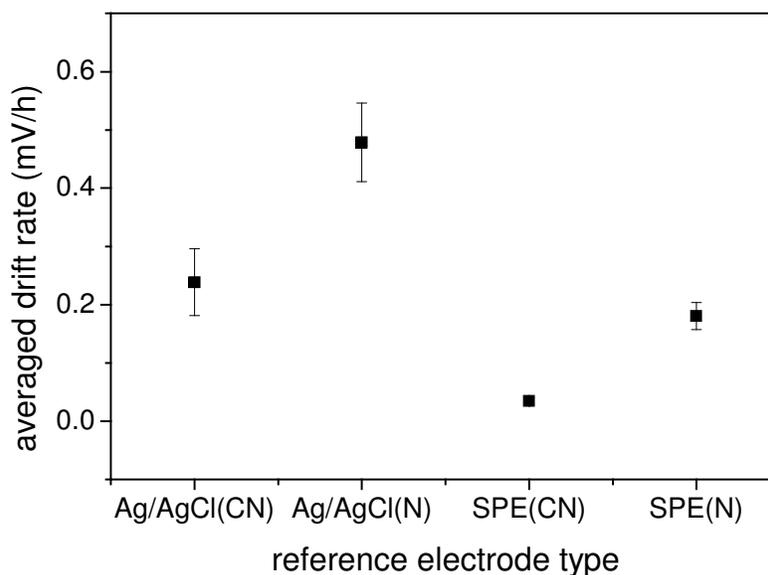


Figure 5. Averaged drift rate of different miniaturised reference electrodes with KCl-containing membrane and protective coating.

The drift rate of the thin-film reference electrodes (type 1) was about 0.2 mV/h for electrodes with a coating of PVC/CN and about 0.5 mV/h for electrodes with a coating of PVC/N. The drift rate of thick-film reference electrodes was smaller (about 0.2 mV/h for electrodes with a coating of PVC/N and less than 0.1 mV for electrodes with a coating of PVC/CN).

The different types of reference electrodes with KCl-containing membranes and a protective layer of PVC/CN or PVC/N were characterised according to their cross-sensitivity towards varying concentrations of chloride ions. The respective calibration curves for changing the concentration of KCl from 10^{-4} M to 10^{-1} M are presented in Fig. 6. It can be seen that independent from the type of the Ag/AgCl layer, the reference electrodes with a coating of PVC/N have a higher sensitivity towards chloride ions than electrodes with a coating of PVC/CN. Using nafion as coating material, a maximum variation of the potential of 16 mV to 21 mV was observed for changing the concentration of the chloride ions from 10^{-4} to 10^{-1} and from 10^{-1} to 10^{-4} , respectively. In contrast, electrodes with CN have only a negligible potential difference of 2 mV to 3 mV in this concentration range.

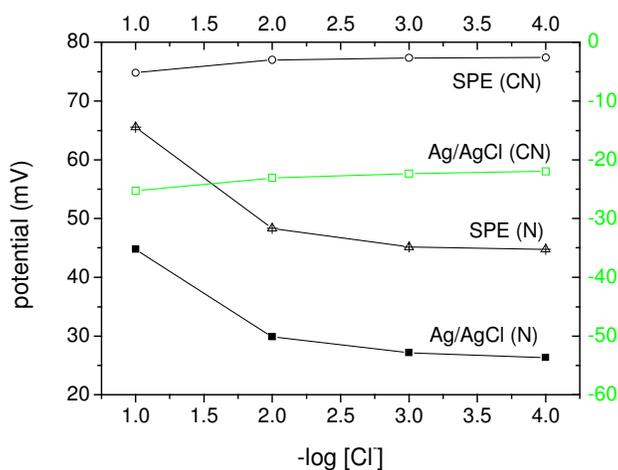


Figure 6. Cross-sensitivity of the miniaturised reference electrodes **with** KCl-containing membrane and protective coating towards chloride ions.

The miniaturised reference electrode fabricated in thick-film technique **without** membrane, was integrated with a thin-film pH sensor on one chip. The electrochemical properties of the pH sensor are described in detail in [13]. Fig. 7 shows a C/V curve of the “one chip” pH sensor. For comparison, a C/V curve of the pH sensor measured with a conventional reference electrode is presented, too. As it can be seen, both curves have a nearly identical shape, however, they are shifted along the voltage axis of about 200 mV. This is not an effect of the integrated system, but of the miniaturised reference electrode itself [12]. The evaluated value of the maximum capacitance is comparable with the calculated value.

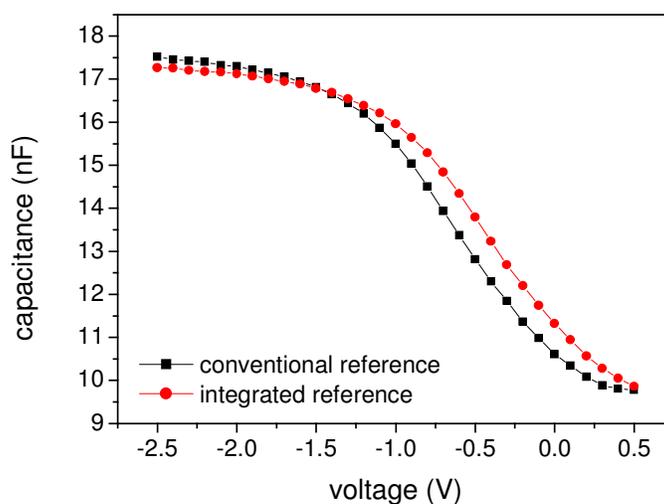


Figure 7. C/V curves of the system pH sensor/integrated reference electrode and pH sensor/conventional reference electrode.

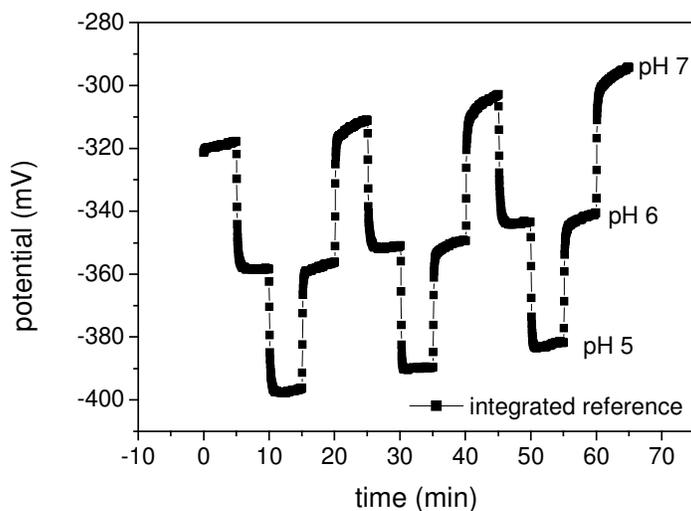


Figure 8. Concap measurement of the system pH sensor/integrated reference electrode.

A preliminary Concap measurement of the “one chip” sensor is demonstrated in Fig. 8. To look over the reproducibility of the measurements, one measurement cycle (pH 7 → pH 5 → pH 7) was repeated for three times. The measurement shows reproducible potentials for each pH value in both directions of changing pH. A slight drift tendency towards the positive potential could be observed when compared with the results of measurements with a hybrid sensor chip [12]. Further measurements are necessary to explain drift phenomenon.

Conclusions

Different strategies have been presented to realise miniaturised reference electrodes by means of well-established thick- and thin-film techniques. The thin-film reference electrodes (evaporation/chlorination) without KCl-containing membrane were stable for 7 hours and the thick-film reference electrodes had a zero potential versus a conventional reference electrode for up to 90 hours in 3 M KCl. The PLD process was not suitable for fabrication of reference electrodes, because the electrodes' stability was only 0.5 hours. To reduce an influence of the chloride ion concentration to the reference electrode and to improve the stability of the potential, the electrodes were additionally covered with a KCl-containing agar agar membrane and a protective coating of PVC/CN or PVC/N. Thus, the reference electrodes of type 1 and type 3 were stable for more than two months in Titrisol, pH 7. The best results could be obtained with thick-film electrodes with a protective coating of CN. The variation of the start potential was less than 4 mV and the drift rate was less than 0.1 mV/h. Independent from the type of the Ag/AgCl layer, the reference electrodes with a coating of PVC/N had a higher cross sensitivity towards chloride ions (variation of the potential of 16 mV to 21 mV) than the electrodes with a coating of PVC/CN (variation of the potential of 2 mV to 3 mV).

The miniaturised reference electrode, fabricated in thick-film technique without membrane, was integrated with a thin-film pH sensor on one chip. The C/V curve of the “one chip” sensor system was

nearly identical to the curve, measured towards a conventional reference electrode. A first Concap measurement of the “one chip” sensor has been performed. The measurement showed reproducible potentials for each pH value in both directions of changing pH. However, a slight drift tendency towards positive potentials could be observed.

The characterisation of the miniaturised reference electrodes, fabricated by means of common fabrication methods in thin- and thick-film techniques, could demonstrate the realisation of electrodes with a stability of more than two months and a low cross-sensitivity towards chloride ions. Further investigations are necessary to characterise the miniaturised reference electrodes according to their cross-sensitivity towards pH. The “one chip” sensor pH/reference will be characterised in detail.

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Sample Availability: Available from the authors.

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