

Universal approach for the fabrication of Ca^{2+} -, K^+ - and NO_3^- -sensitive membrane ISFETs

P.D. van der Wal*, A. van den Berg and N.F. de Rooij

University of Neuchâtel, Institute of Microtechnology, Rue A.-L. Breguet 2, CH-2000 Neuchâtel (Switzerland)

Abstract

A new method to functionalize silanol-terminated polysiloxanes is presented. The method can be used for the realization of tailor-made ion-selective membranes. A siloxane copolymer containing polar cyano groups combined with a condensation-type cross linking overcomes the earlier encountered problem of high membrane resistance. After modification of this material with methacrylate groups, a photocurable polysiloxane was obtained. Potassium- and calcium-selective ISFETs with excellent sensitivities and selectivities ($\log K_{K,i} < -3.5$, $i = \text{Na}^+$, Mg^{2+} , Ca^{2+} ; $\log K_{\text{Ca},i} < -3.2$, $i = \text{Na}^+$, K^+ , Mg^{2+}) could be made with this material using photolithography. Also quaternary ammonium ion-exchange groups could be coupled to the polymer using the same technique. Using this modified polysiloxane we have been able to realize nitrate-sensitive ISFETs with a slope of 57-58 mV/decade, and a selectivity versus Cl^- of $\log K_{\text{NO}_3, \text{Cl}} = -2$.

Introduction

Since the introduction of the ion-sensitive field-effect transistor (ISFET) many efforts have been made to realize other ion-sensitive devices through the deposition of ion-sensitive membranes. However, none of the approaches presented up to now has combined a photolithographically structured membrane with the chemical attachment of the membrane to the ISFET surface as well as the chemical immobilization of the ion-sensitive components in the membrane. These aspects are indispensable for the creation of durable multi-sensors that can be mass-fabricated.

Up to now, the method most frequently used to fabricate ion sensors, for ions other than H^+ , is to dip-coat the ISFETs with a plasticized, ionophore-loaded, PVC membrane. This dip-coating is usually carried out by immersing the encapsulated ISFET one or several times in a diluted solution of the membrane material in THF. This method, published for the first time in 1975 by Moss *et al.* [1], has several disadvantages such as bad adhesion, leaking out of plasticizer, poor reproducibility and, above all, incompatibility with on whole-wafer fabrication techniques.

For some of these problems, separate solutions have been proposed like using a suspended mesh [2], chemically modified PVC [3], and the use of alternative membrane materials like silicones [4].

Recently, we have reported the use of a photocross-linkable polysiloxane which allows an appropriate thickness control of the membrane and an on-wafer applicable deposition [5]. Unfortunately, a disadvantage of these membranes is the relatively high electrical impedance giving rise to unstable sensor signals.

We present here a universal strategy for the realization of photopolymerizable tailor-made siloxane membranes. As base material, silanol-terminated polysiloxanes are used similar to the ones presented earlier [6], that can be modified with methacrylate groups through a condensation reaction. The proposed approach opens the possibility to use a large variety of commercially available silanol-terminated polysiloxane materials with various kinds of physicochemical properties. The use of cyano-functionalized base material, coupled with the described combined cross-linking technique overcomes the earlier encountered problem of high membrane resistance. With the described method we have been able to realize calcium- and potassium-sensitive ISFETs using photolithography. With the functionalization method described above a variety of silylating agents can be used to modify silanol-terminated polysiloxanes. The method has been used to modify a polysiloxane with quaternary ammonium groups. With this modified polysiloxane we have been able to realize nitrate-sensitive ISFETs.

Experimental

Chemicals

All metal salts used were of p.a. grade (Merck). Calcium ionophore ETH 5234, valinomycin, potassium

*Author to whom correspondence should be addressed.

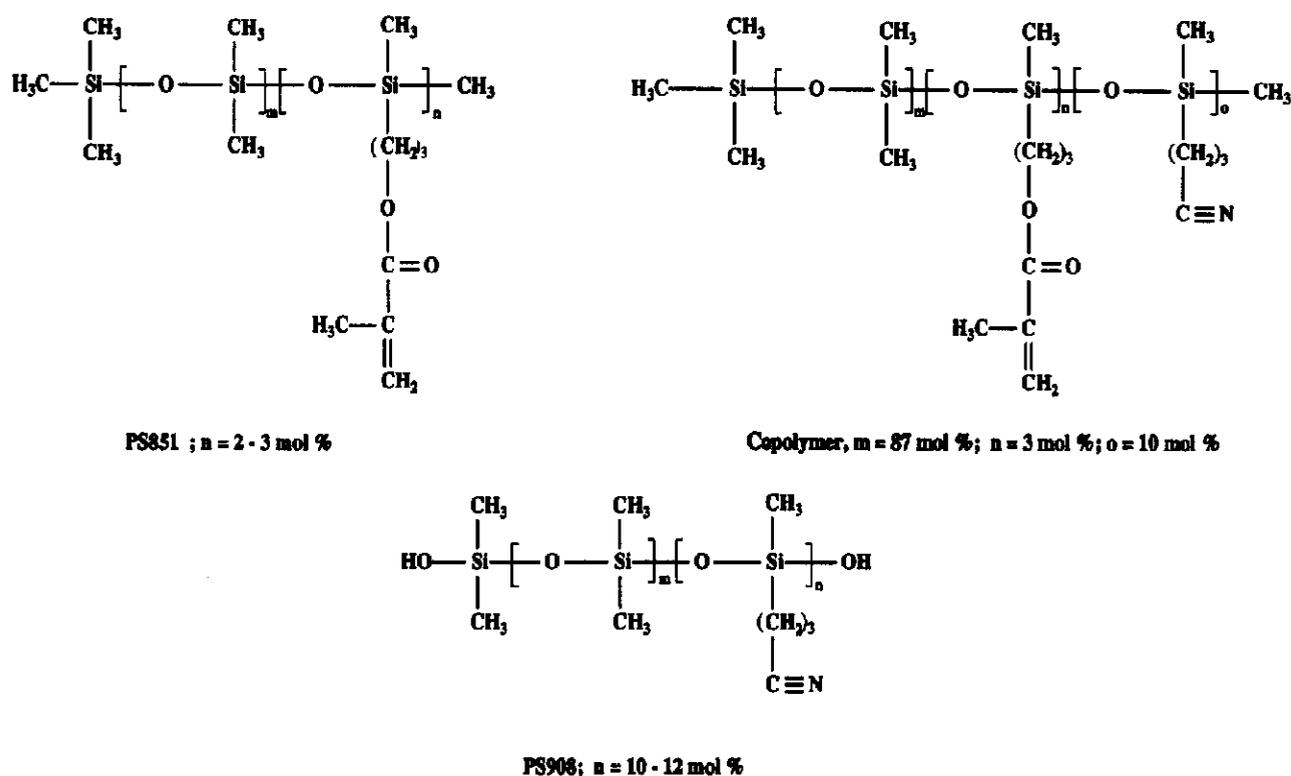


Fig. 1. Structure of the investigated siloxane polymers.

tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, and Siloprene cross-linking agent K-11 were purchased from Fluka. The polysiloxanes PS851 (2–3%)methacryloxypropyl(methyl)(97–98%)-dimethyl siloxane copolymer, PS908 (10–12%)cyanopropyl(methyl)(88–90%)-dimethyl siloxane copolymer, PS2067 (polyfunctional acrylate siloxane), and silane T2925 (trimethoxysilylpropyltrimethylammonium chloride, 50% in MeOH) were purchased from ABCR, methacryloxypropyltrimethoxysilane (MPTMS) from Aldrich; the random copolymer of 10% cyanopropyl(methyl)3% methacryloxypropyl(methyl) and 87% dimethyl siloxane was a gift from the Organic Chemistry group, Twente University, The Netherlands. The structures of the polysiloxane materials are given in Fig. 1, the structures of the silanes used for modification of PS908 are given in Fig. 2.

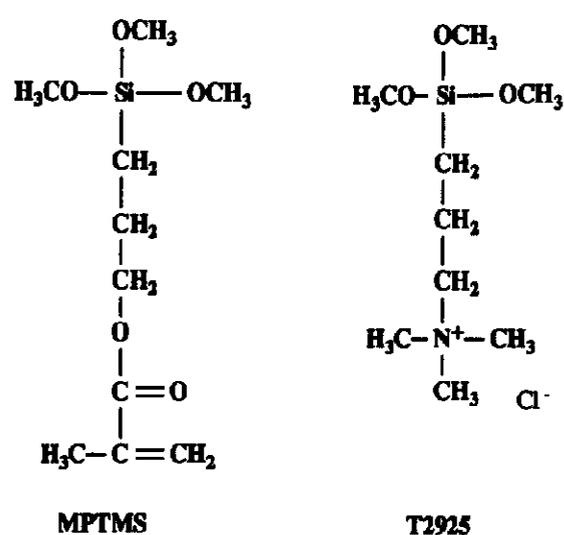


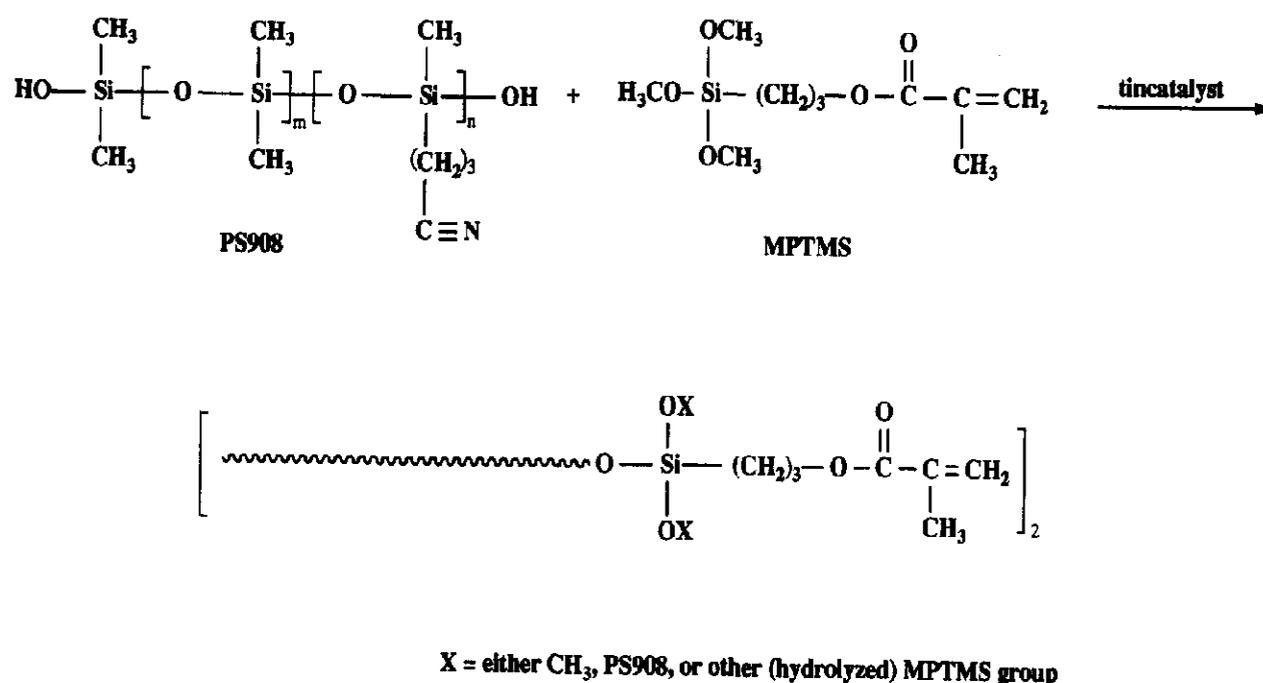
Fig. 2. Structure of the silane reactants.

Chemical modification of PS908

A typical example of the synthesis of modified PS908 is given below and is visualized in Scheme 1. 200 mg of PS908, 20 mg methacryloxypropyltrimethoxysilane (MPTMS, Aldrich), 2 mg photoinitiator (2,2'-dimethoxyphenylacetophenone, Aldrich) and 2 mg dibutyltindilaurate (Aldrich) were dissolved in 0.2 ml of methylene chloride. After homogenizing, the mixture was allowed to stand overnight at room temperature in a brown glass bottle. In most cases, the ionophore and tetraphenylborate salt were added directly to the reaction mixture. The addition of both components after completion of the condensation reaction had no noticeable effect on the cross-linking reaction or sensor properties. For photolithographic applications 20 mg of the polyacrylate siloxane PS2067 was added to the reaction mixture. This was necessary to withstand the swelling action of the developing solvents. The reaction mixture used for making anion-sensitive ISFETs contained 2 mg of T2925 solution. This was added to the mixture containing MPTMS, or two solutions (one with MPTMS and one with T2925) were made and mixed in the appropriate ratios later.

Membrane deposition

The ISFETs used in this work had the same basic structure as described in ref. 5. The dimensions were 2.0 mm × 0.75 mm. Prior to the membrane deposition, the wafers were silylated with MPTMS. The membranes used here on ISFETs contained approximately 1 wt.% ionophore with 40–50 mol% potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. For the membrane resistance measurements, the membrane mixture was deposited on encapsulated ISFETs. The solvent was



Scheme 1. Reaction scheme for the chemical modification of the silanol-terminated PS908 polysiloxane.

allowed to evaporate during at least 5 min. Then the ISFETs were photocured in a nitrogen-purged glass tube under a UV lamp. Photolithographic experiments were performed on whole or quarter ISFET wafers. The UV cross-linking was carried out under a Mylar™ film during 3 min. The material was developed in two steps using xylene and isopropanol. The ISFETs were then left in air for at least 24 h to complete the condensation cure reaction. During this period it was noticed that the material becomes slightly harder and stronger. The membranes had dimensions of 400 μm × 600 μm, the patterning could be performed with a good resolution of approximately 20 μm with a membrane thickness varying between 40 and 70 μm. After wafer-cutting, the ISFETs were mounted on printed circuit boards and encapsulated. Although normally the encapsulation material was epoxy resin, in some cases RTV 3140 (Dow Corning) silicone rubber was used. The response and selectivity of sensors with the different membrane modifications were tested in chloride solutions (cation sensors) and in potassium solutions (anion sensors) using the separate solution method for determination of the selectivities.

Membrane resistance

The membrane resistance was quantified indirectly by measuring the a.c. transconductance of a membrane-covered ISFET. This was performed in the following measuring setup: an ISFET and a reference electrode are immersed in a 0.1 M calcium chloride solution. Both are connected to a power source. The drain-source voltage V_{DS} was set on 1 V and the drain current I_d was 30 μA. With a function generator an a.c. signal is applied via the reference electrode to the gate of the ISFET. The drain current is monitored with an

oscilloscope. The frequency of the a.c. signal is increased from less than 1 Hz to 10 kHz (maximum).

The voltage drop of the applied a.c. signal is divided over the series connection of ISFET-oxide capacitance (C_{ox}) and membrane resistance and capacitance (C_{mem}). At low frequencies, the whole a.c.-voltage drop takes place over the oxide, at high frequencies it is divided over C_{mem} and C_{ox} (normally C_{ox} is more than 100 times higher than C_{mem}). The frequency at which the amplitude of the drain current reached half the value measured at low frequency, was chosen as an indication for the membrane resistance. Membrane thicknesses were estimated with a microscope. The mean value was taken of the thickness measured at the top and the bottom of the gate. The frequencies in Table 1 are standardized for a standard thickness of 100 μm.

TABLE 1. Indirect measurement of the membrane resistance: frequencies are normalized for 100 μm thickness, the higher the frequency, the lower the resistance (see Experimental)

| Membrane ^a | Immersion time (days) | | | |
|------------------------|-----------------------|-----------|---------|-------|
| | 0 | 1 | 7 | 14 |
| PS851 | 1-5 | | | |
| PS851 ^b | 60-80 | | | |
| Copolymer ^c | 100-110 | 55 | 55 | 50-55 |
| PS908 ^d | 1000 | 300-500 | 150 | 145 |
| PS908 ^e | 400-700 | 200-300 | 160-180 | |
| PVC/NPOE | 1500-2000 | 1600-2500 | | |

^aAll membranes with 1 wt.% calcium ionophore ETH 5234 and 40-50 mol% KB[Φ(CF₃)₂]₄, unless stated otherwise.

^bNo ionophore.

^cRandom copolymer of methacryloxypropyl(methyl)cyanopropyl(methyl)dimethyl siloxane.

^dCross-linked via a condensation reaction using K-11.

^eCross-linked via both a radical reaction and a condensation reaction.

Results and discussion

Membrane resistance

Earlier we have shown that a copolymer of methacryl(methyl) and dimethyl siloxane (PS851) can be deposited and patterned on wafer by using photolithographic techniques [5]. The adhesion of the membrane to the oxide substrate is very good when the substrate is treated with an appropriate silylating agent. ISFETs with these patterned membranes, containing a calcium ionophore (ETH 129) and potassium tetrakis(4-chlorophenyl)borate showed a good calcium sensitivity and selectivity. Also the patterning could be performed with a good resolution of 20 μm with a membrane thickness of 50 μm . However, due to the apolar nature of the polysiloxane membrane material, the concentration of dissociated salts in the membrane is low. This leads to a high membrane resistance and the resulting sensor suffers from a relatively high noise level (several mV).

Our research has therefore been focused on the increase of the conductivity of photopolymerizable polysiloxane membrane materials. This can be achieved in two ways. Firstly by using more lipophilic membrane components having a better compatibility with the apolar membrane and secondly by the development of a more polar membrane material. In order to measure the membrane resistance in an easy and fast way, a special method was developed to measure the relative resistance of the membrane material. This was possible with the membrane mounted on the encapsulated ISFET (see Experimental; the theoretical background of this method has been described in ref. 7). Several different polysiloxane membranes containing the calcium ionophore ETH 5234 and potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($\text{KB}[\Phi(\text{CF}_3)_2]_4$) were measured with this method. Both membrane components are more lipophilic than the components mentioned above and improved the membrane resistance slightly. In Table 1 the relative membrane resistance of several calcium-selective polysiloxane membranes is given. All membrane modifications showed roughly the same behavior: a linear near nernstian calcium response from 10^{-5} to 10^{-1} M CaCl_2 and a good selectivity (selectivity coefficients $\log K_{\text{Ca}, \text{Na}} = < -3.5$, $\log K_{\text{Ca}, \text{K}} < -3.5$, $\log K_{\text{Ca}, \text{Mg}} < -4$).

It is interesting to see that the membrane conductivity of a membrane containing only the lipophilic salt is rather good. However, addition of the ionophore reduces the conductivity by a factor 10 to 60. Obviously, the cation is the main contributor to the conductivity and after lowering of the mobility by complex formation, the conductivity greatly decreases. This effect has been described before in ref. 8.

Cyano-modified polysiloxanes

A method to increase the dielectric constant ϵ is the incorporation of highly polar cyano groups in the siloxane polymer [6, 9]. In ref. 6 the membrane resistance of several siloxane copolymers is reported, measured with the a.c. impedance method. In this paper, the effect of the cyano groups was confirmed; in addition it was shown that the cross-linking mechanism has also an influence on the membrane resistance.

A random copolymer of 10% cyanopropyl(methyl), 3% methacryloxypropyl(methyl) and 87% dimethyl siloxane was tested. ISFETs with this membrane showed a good calcium response, whereas the membrane resistance was at least 10 to 50 times lower than the PS851 membrane resistance (see Table 1). PS908 is a commercially available copolymer containing 10 to 12% cyanopropyl(methyl) siloxane and 88–90% dimethyl siloxane. The polymer can be cross-linked via a condensation reaction of the silanol endgroups with Siloprene cross-linking agent K-11. The cross-linking mechanism is identical to the cross-linking mechanism of the membrane material Siloprene [4]. The PS908 membranes cross-linked with K-11 have even a lower resistance than membranes made from the random copolymer, mentioned above. Although the membrane resistance initially increases rapidly after the membrane is immersed in the electrolyte solution, its final value is approximately 3 times lower than the resistance of the random copolymer. The origin of the increase of the resistance is not yet clear. The high conductivity might be partially caused by the slow liberation of reaction products (i.e., alcohol) of the condensation reaction and as this reaction finishes the resistance might increase again. For comparison, in Table 1 the values measured for a calcium-sensitive plasticized PVC membrane are also given. Directly after immersion the resistance of the PS908 membranes is only twice as large as the resistance of the PVC membranes. After this initial period the resistance of the PS908 increases to a value that is 15 to 20 times as large as the initial PVC membrane resistance. The latter decreases slightly upon exposure to electrolyte solutions.

In order to make the PS908 copolymer photopolymerizable a methacrylate group was introduced into the polymer. Using the same condensation reaction as mentioned above, the silanol endgroups could be modified with MPTMS (see Scheme 1). The resulting polymer can be cross-linked via both a moisture-induced condensation of silanol with alkoxy silane groups, and via a photochemically initiated radical reaction of the methacrylate groups. Moreover the formulation of the reaction mixture had to be optimized so that the condensation cross-linking reaction was slow enough to perform photolithography. With the optimized mixture well-defined structures can be made on wafer,

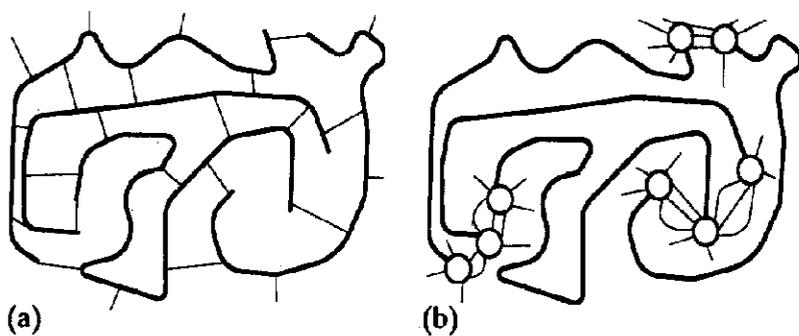


Fig. 3. Schematized drawings of cross-linked membrane materials: (a) random copolymer with cross links evenly divided over the polymer chain; (b) block copolymer with cross-linked areas.

comparable with the structures made before with PS851, see below. As can be seen from Table 1, the membrane resistance of the photopolymerized membranes is similar to the resistance of membranes cross-linked only via the condensation reaction. Also the increase of the membrane resistance after immersion is similar.

The difference in membrane resistance between the photopolymerizable random copolymer and our modification is interesting. In ref. 6, the influence of the cross-linking mechanism on the membrane resistance has already been described. Cross-linking of a random siloxane copolymer containing cyano- and methacrylic groups via a condensation reaction of the silanol end-groups resulted in a membrane with a lower resistance than cross-linking of the same copolymer via a radical reaction of the methacrylic groups. The siloxane block copolymer described here combines both cross-linking mechanisms. In the random copolymer described above, the cross links are more or less evenly divided over the polymer chain. In our membrane modification, however, the chain length between the cross links is much longer (see Fig. 3). In other words, the meshes of the cross-linked polymer are bigger which can result in a higher mobility of the ions.

Photolithographic experiments

Calcium- and potassium-selective membranes were made on ISFET wafers using photolithography. Potassium sensors were made using valinomycin and calcium sensors using ETH 5234. The membrane resistance of both types was slightly higher compared with the membranes that were deposited and photopolymerized on encapsulated ISFETs. Clearly, some of the electroactive material is lost during the development steps.

The sensitivity and selectivity of the potassium sensors slightly increased in the first days after immersion in KCl solutions. After this conditioning period the sensors had a slope of 54 to 55 mV/dec. Selectivities towards Na^+ , Mg^{2+} , and Ca^{2+} were good ($\log K_{K,i} < -3.5$). A second photolithographic step with the mixture containing the calcium ionophore could also be performed with the same high resolution. After this treatment the potassium sensors still showed a good K^+ selectivity,

obviously no contamination with the calcium ionophore has taken place. This result is encouraging for the manufacture of multisensors using photolithography. Unfortunately, the membrane resistance has further increased resulting in high noise levels (few mV).

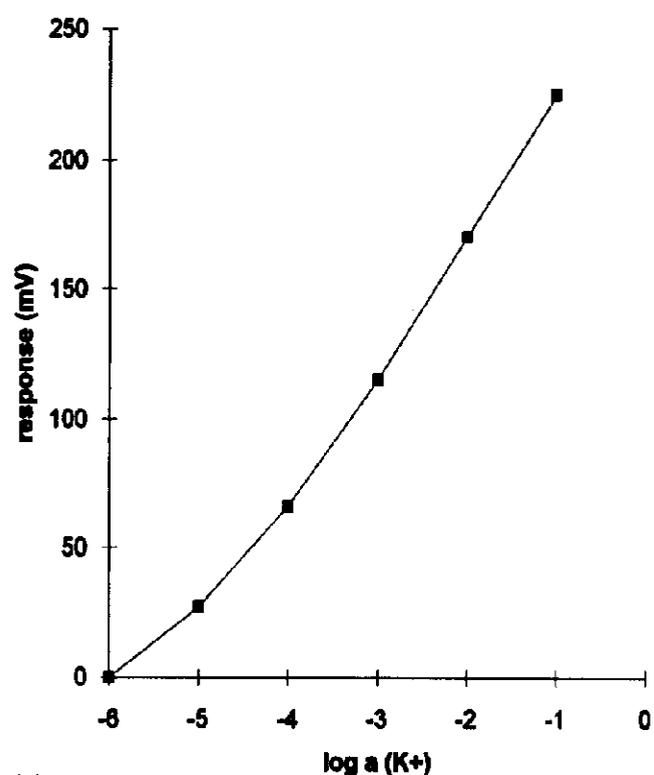
The manufacture of calcium sensors was more troublesome. After the membrane deposition the ISFETs were wire-bonded and encapsulated according to the normal procedure using epoxy resin. However no calcium-sensitive devices could be obtained in this way. Encapsulation of the devices with silicone rubber yielded calcium-sensitive devices with a good sensitivity in CaCl_2 solutions. Selectivities towards Na^+ , K^+ , and Mg^{2+} were not as good as with the experiments on encapsulated ISFETs mentioned above, but were still satisfactory ($\log K_{\text{Ca},i} < -3.2$). Obviously the use of epoxy resin and curing at 80 °C has a disastrous effect on the calcium ionophore. Perhaps this effect is caused by amine fumes released by the epoxy resin. It was also observed that the durability of these silicone encapsulated sensors was not very good, after 2 to 3 weeks of continuous immersion the calcium selectivity was greatly reduced. During the decrease of the selectivity it was noticed that the sensor displayed a growing pH sensitivity. As sensors with only $\text{KB}[\Phi(\text{CF}_3)_2]_4$ showed a large pH effect, it is suspected that the calcium ionophore either leaches out of the membrane or slowly degrades, resulting in excess anionic sites.

A typical response curve of the K^+ and Ca^{2+} with photolithographically deposited membranes is shown in Fig. 4. In Fig. 5, a SEM picture shows a finished multisensor, with one pH and two membrane modified ISFETs, made in two photolithographic steps.

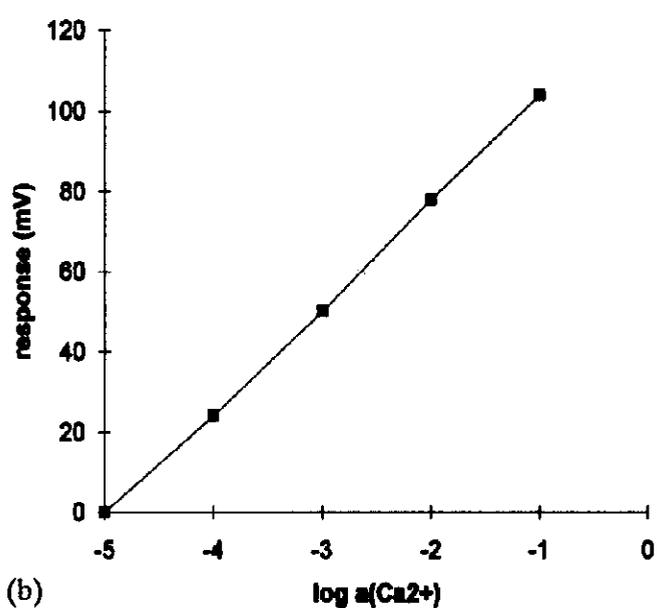
During all the experiments described above, only 1 wt.% of ionophore was used. Higher loading of the membrane might result in a higher remaining ionophore concentration after the development steps which is beneficial for the sensor durability. The use of electroactive components chemically bound to the membrane matrix is of course a better solution. For the manufacture of multisensors, to prevent contamination of other membranes, these components should be polymer-bound before the final cross-linking reaction. With the siloxane modification method described here it is possible to covalently bind electroactive components to the siloxane backbone. As an example the modification of PS908 with an anion exchanger is reported below.

Nitrate-sensitive ISFETs

Conventional nitrate-ion-selective electrodes are based on quaternary ammonium salts dissolved in plasticized PVC. Although the selectivity of this type of sensor is restricted to the Hofmeister lyophilic series, nitrate-ion-selective electrodes have gained widespread use.



(a)



(b)

Fig. 4. Response curve of ISFETs with photolithographically deposited membranes; (a) K⁺ sensor; (b) Ca²⁺ sensor.

To show the versatility of the method described to functionalize polysiloxanes, we investigated the modification of PS908 with a silylating agent containing a quaternary ammonium salt: trimethoxysilylpropyltrimethylammonium chloride silane (T2925). Using this method the ion exchanger will be chemically bound to the membrane matrix. Moreover, it should be possible to deposit the membranes using photolithographic techniques. In the literature some membranes are reported with ion-sensing groups covalently attached to the polymer matrix [10, 11]. Especially a poly-(trioctylvinyl)benzylphosphonium nitrate membrane electrode showed good properties [11]. However this material cannot be deposited using photolithography. The photolithographic deposition of a plasticized acrylate membrane containing a quaternary phosphonium salt on thin-film electrodes is also reported [12]. The performance of this sensor was not as good as plasticized

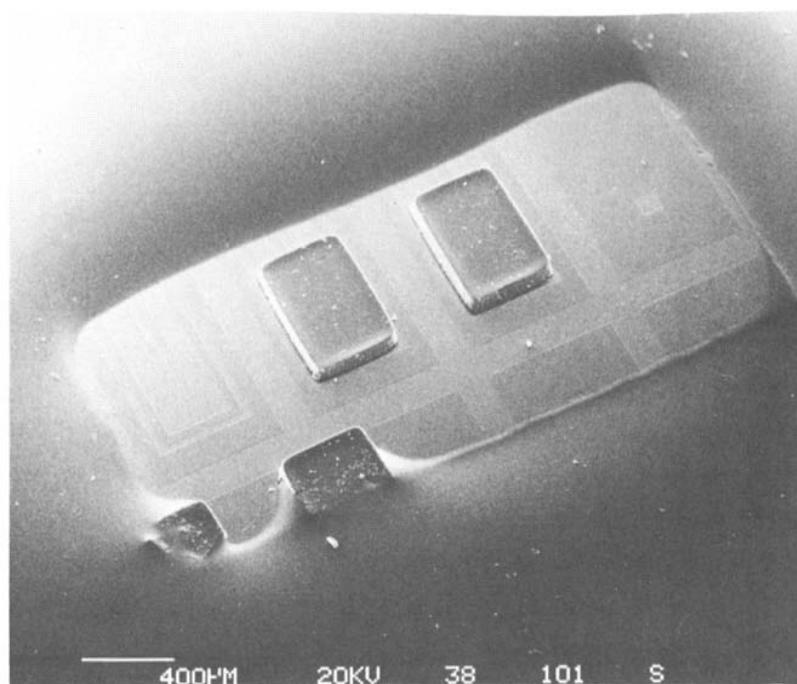


Fig. 5. SEM micrograph showing photolithographically structured membranes on top of encapsulated ISFETs.

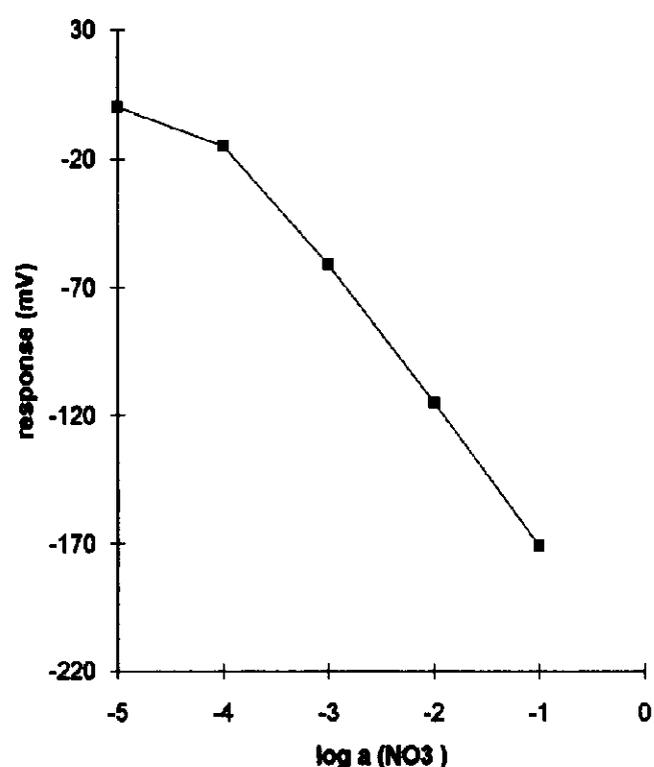


Fig. 6. Response curve of nitrate-selective ISFET.

PVC membranes but still satisfactory, with a lifetime of over 2 months. However, for long lifetimes the presence of membrane components that can leak out of the membrane should be avoided.

Approximately 0.8 to 1 wt.% of T2925 was added to the PS908 reaction mixture (also containing MPTMS). The addition of higher amounts of T2925 resulted in inhomogeneous membranes. Membranes were deposited on encapsulated ISFETs. After curing, the membranes were conditioned overnight in a 0.1 M KNO₃ solution. ISFETs modified in this way did show a good anion sensitivity and NO₃⁻ selectivity. A typical response curve is given in Fig. 6, the response curve is linear from almost 10⁻⁴ to 10⁻¹ M (highest concentration measured) with a slope of 57–58 mV/decade.

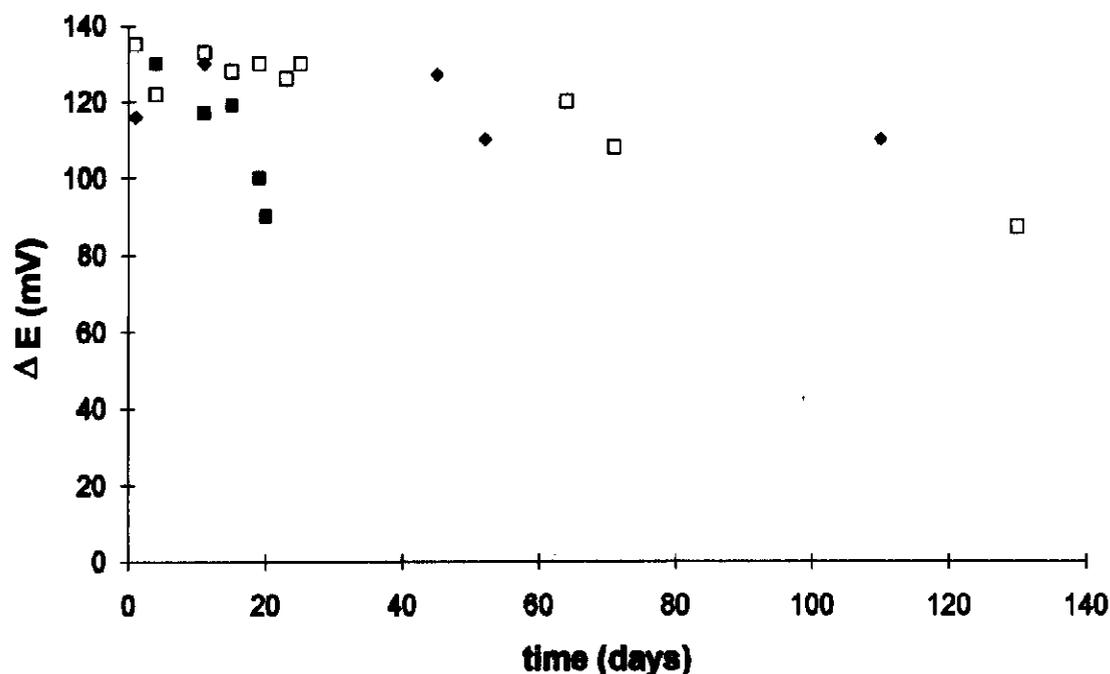


Fig. 7. Evolution of three identical nitrate-selective sensors, potential difference between 0.1 M KCl and KNO_3 solutions: ■, defective after 20 days; □, ◆, still functioning after 4 months.

Selectivities measured with the separate solution method are: $\log K_{\text{NO}_3, \text{SO}_4} = -2.8$, $\log K_{\text{NO}_3, \text{Cl}} = -2$, and $\log K_{\text{NO}_3, \text{Br}} = -0.8$. The durability of these sensors was tested by monitoring the potential differences between 0.1 M KNO_3 and KCl solutions (see Fig. 7). The durability of these sensors was very good, after approximately 2 months the NO_3/Cl selectivity was still $\log K_{\text{NO}_3, \text{Cl}} = -1.9 \pm 0.1$, after 4 months the selectivity had slightly decreased to $\log K_{\text{NO}_3, \text{Cl}} = -1.5$.

It has to be emphasized, however, that the optimum experimental conditions are quite critical, in the next series of experiments, some sensors suffered from a lower NO_3/Cl selectivity ($\log K_{\text{NO}_3, \text{Cl}} = -1.7 \pm 0.3$) and higher noise levels. Our research on this subject made clear that the cross-linking mechanism, and especially the effect of moisture on the condensation-cure reaction is crucial for the resulting sensor behaviour. It is suspected that the condensation reaction influences the accessibility of the ion-exchange sites.

The T2925-modified membrane material could be deposited photolithographically on wafer with the same resolution as described above. Unfortunately, preliminary measurements showed that the electrochemical behaviour of these sensors was not satisfactory: only a slight NO_3/Cl selectivity could be observed. Our further research in this area will first concentrate on the elucidation of the cross-linking mechanism, the understanding of which will be beneficial for the further development of the photolithographic deposition of nitrate-selective membranes.

Conclusions

The new method of polysiloxane modification reported here has proved to be a relatively easy and

versatile method of introducing a desired functionality in a siloxane polymer. It can be used for the functionalization of different types of silanol-terminated polysiloxanes with almost any silylating agent. The main restriction of this method is the solubility of all reaction compounds in the chosen solvent. Using this method, a commercial cyano groups containing polysiloxane could be modified with methacrylate groups. This polar membrane material had a much higher conductivity compared with the apolar polysiloxane PS851 as could be measured with the membranes mounted on the chip. Further, it was found that the block copolymer formed in this way has a slightly better conductivity compared with a random copolymer.

With the new membrane material calcium- and potassium-selective ISFETs sensors could be made using photolithography. The manufacture of multisensors with photolithography, however, seems to be limited because of the loss of electroactive material during the development steps which again causes high noise levels.

The loss of electroactive material can be circumvented by chemically binding these species to the membrane matrix. Therefore, our modification method was used to functionalize the polysiloxane with a quaternary ammonium salt. ISFETs provided with this membrane material showed a good nitrate selectivity, comparable with conventional ion exchange-type nitrate-selective electrodes. For the photolithographic deposition of this material further research is in progress.

Acknowledgements

The financial support of Microsens SA during the initial phase of this work and the technical assistance

of J.D. Cretin (Microsens SA) and S. Pochon (Institute of Microtechnology) is gratefully acknowledged.

References

- 1 S.D. Moss, J. Janata and C.C. Johnson, Potassium ion-sensitive field-effect transistor, *Anal. Chem.*, **47** (1975) 2238.
- 2 C.F. Blackburn and J. Janata, The suspended mesh ion-selective field-effect transistor, *J. Electrochem. Soc.*, **129** (1982) 2580.
- 3 D.J. Harrison, A. Tecler and L.L. Cunningham, *Proc. 4th Int. Conf. Solid-State Sensors and Actuators (Transducers '87), Tokyo, Japan, June 2-5, 1987*, p. 768.
- 4 P.D. van der Wal, M. Skowronska-Ptasinska, A. van den Berg, P. Bergveld, E.J.R. Sudhölter and D.N. Reinhoudt, New membrane materials for potassium-selective ion-sensitive field-effect transistors, *Anal. Chim. Acta*, **231** (1990) 41.
- 5 A. van den Berg, A. Grisel and E. Verney-Norberg, An ISFET-based calcium sensor using a photopolymerized polysiloxane membrane, *Sensors and Actuators B*, **4** (1991) 235.
- 6 P.D. van der Wal, E.J.R. Sudhölter, B.A. Boukamp, H.J.M. Bouwmeester and D.N. Reinhoudt, Impedance spectroscopy and surface study of potassium-selective silicone rubber membranes, *J. Electroanal. Chem.*, **317** (1991) 153.
- 7 P. Bergveld, A. van den Berg, P.D. van der Wal, M. Skowronska-Ptasinska, E.J.R. Sudhölter and D.N. Reinhoudt, How electrical and chemical requirements for REFETs may coincide, *Sensors and Actuators*, **18** (1989) 309.
- 8 R.D. Armstrong and M. Todd, Ionic mobilities in PVC membranes, *Electrochim. Acta*, **32** (1987) 155.
- 9 O.H. Leblanc, Jr. and W.T. Grubb, Long-lived potassium ion-selective polymer membrane electrode, *Anal. Chem.*, **48** (1976) 1658.
- 10 L. Ebdon, J. Braven and N.C. Frampton, Nitrate-selective electrodes with polymer membranes containing immobilised sensors, *Analyst*, **115** (1990) 189.
- 11 M.J. Rocheleau and W.C. Purdy, Ion-selective electrode with fixed quaternary phosphonium ion-sensing species, *Analyst*, **117** (1992) 177.
- 12 C. Dumschat, R. Frömer, H. Rautschek, H. Müller and H.J. Timpe, Photolithographically patternable nitrate-sensitive acrylate-based membrane, *Anal. Chim. Acta*, **243** (1991) 179.