

STUDY OF FRONT-SIDE CONNECTED CHEMICAL FIELD EFFECT TRANSISTORS FOR WATER ANALYSIS

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ABSTRACT: Front-side connected, N-channel, normally-off, chemical field effect transistor (ChemFET) microsensors including a $\text{SiO}_2/\text{Si}_3\text{N}_4$ pH-sensitive gate have been fabricated using a standard P-well silicon technology. The fabrication and packaging processes are described and sensor properties and performances are demonstrated through pH measurements. Finally, the front-side connected ChemFETs microsensors have been adapted to the detection of ions thanks to polyHEMA/siloprene-based ionosensitive membranes. Application is performed through the NH_4^+ and NO_3^- ions detection in artificial solutions, evidencing quasi-Nernstian responses ($s \approx 50 \text{ mV/pH}$) in the appropriate detection ranges. This microsensor will be used for the monitoring of environmental pollution and more precisely for ground water analysis.

INTRODUCTION

The monitoring of the environment pollution requires the development of smart, miniaturised chemical sensors for water analysis. This goal should be reached by using the silicon microtechnologies in order to fulfil the need for mass-fabrication. In this context, the chemical field effect transistors (ChemFETs) have become an excellent candidate for the industrial development of chemical microsensors [1]. As a solid-state sensor deviated from microelectronics, it provides many advantages like compatibility with silicon technology, mass fabrication, low cost and low power, and has been used for the detection of many ions thanks to many ionosensitive membranes [2-7].

According to the water analysis market, a low-cost technology for simple, general-public applications and a higher-cost, enhanced performances technology for more complex and more specialised applications have to be developed. This goal will be respectively reached through the conception, the fabrication and the optimisation of front-side connected (FSC) and back-side-connected (BSC) ChemFETs. The FSC design uses a simpler technological process and required an optimised encapsulation whereas the BSC one eliminates the necessity of encapsulation through the construction of specialised flow cells [8]. Nevertheless, whatever the technology, the development strategy should take into account the conception of a ChemFET generic structure, its specification according to the mass-fabricated ionosensitive layers and the development of a specific packaging adapted to the final applications.

This paper deals with the development of the low-cost, front-side connected ChemFET technology for water analysis and more precisely for the detection of the H^+ , NH_4^+ and NO_3^- ions in aqueous solutions.

EXPERIMENT

Sensors technology

Ion sensitive field effect transistors (ISFETs) were fabricated on $\langle 100 \rangle$ -oriented, N-type ($500 \text{ } \Omega \cdot \text{cm}$) silicon substrate. The insulation between the electrical active zones and the electrolyte was performed using a standard P-well technology, leading to the fabrication of N-channel, normally off ISFETs (figure 1). A 50nm thermally grown SiO_2 layer and a 50nm Si_3N_4 layer deposited on top formed the pH-sensitive gate structure. All in all, taking into account the P-well and the dielectric gate technological processes and characteristics, the pH-ISFET microsensor was optimised in order to have a threshold voltage V_t lower than 1 volt.

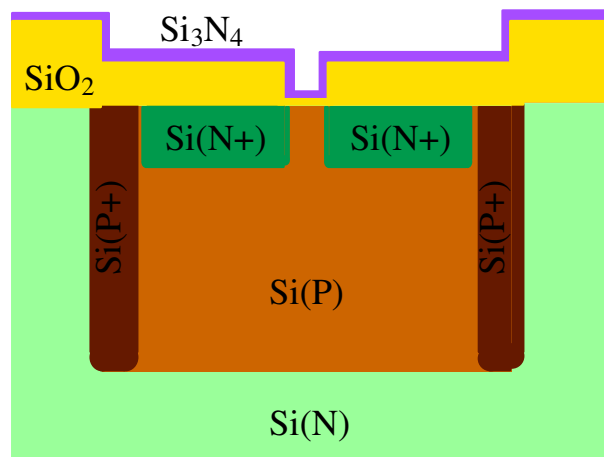


Figure 1. cross section of the front-side connected, P-well, N channel, ChemFET microsensors

Chemicals

pH measurements were performed for standard solutions purchased from Merck. The NH_4^+ and NO_3^- ions detection was characterised using different aqueous solutions of ammonium nitrate NH_4NO_3 (purchased from Fluka).

The 3-(trimethoxysilyl)propyl methacrylate (MPTS), the ionophores (nonactine for the NH_4^+ ion, tetradodecylammonium nitrate for the NO_3^- ion), the potassium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (KTFBP) lipophilic salt, the siloprene K1000 and its crosslinking agent, and the tetrahydrofuran THF used for the fabrication of the ionosensitive layers were also purchased from Fluka.

Development of the ionosensitive layers

The front-side connected ChemFET applications have been extended to ion detection thanks to siloprene-based ionosensitive membranes. The deposition process has been performed using a recipe given by the Warsaw University of Technology [9]. To reduce interference with the solution pH, an underlying membrane should be added. One well-known membrane for this application is the poly hydroxyethyl methacrylate (polyHEMA). After a pre-silanisation step using 3-(trimethoxysilyl)propyl methacrylate (MPTS), a 25-micron thick, patterned polyHEMA film has been deposited on top of the $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectric gate using spin coating and photolithography techniques (figure 2) [10]. Finally, the siloprene-based ionosensitive layers were deposited by dip coating on the polyHEMA film [9].

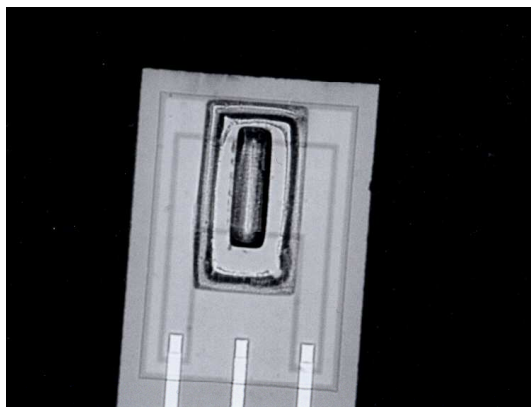


Figure 2. Photograph of the ChemFET $\text{SiO}_2/\text{Si}_3\text{N}_4$ pH-sensitive gate covered by the polyHEMA membrane and protected by the polysiloxane O-ring

Sensors packaging

The 2 x 5 square millimetres ChemFET chips (figure 3) were reported on a specific printed circuit board. After wedge wire bonding, they were encapsulated with epoxy resin by dispensing while using an O-Ring polymer

membrane to protect the ionosensitive gate (figure 2). The packaged FSC-CHEMFETs prototypes are finally represented on figure 4.

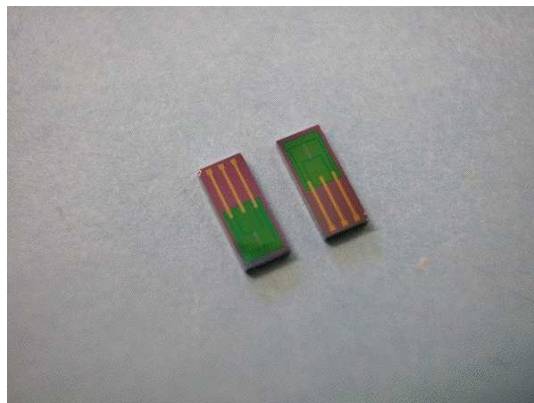


Figure 3. Photograph of the FSC-ChemFET silicon chip



Figure 4. Photograph of the encapsulated FSC-ChemFET microsensors

Measurements

The gate-source voltage being applied to the solution versus a reference calomel electrode, ISFETs chemical sensors were characterised for a constant drain-source current $I_{\text{DS}} = 0.1 \text{ mA}$ and drain-source voltage $V_{\text{DS}} = 2 \text{ V}$, the P-well being connected to the source and the substrate being not connected. All the measurements were done at room temperature.

RESULTS

FSC-ChemFET microsensors validation by pH measurements

The performances of the $\text{SiO}_2/\text{Si}_3\text{N}_4$ front-side connected ChemFET generic microsensors have been studied through pH measurements. Good electrical characteristics have been evidenced in agreement with the threshold voltage ($V_t < 1 \text{ V}$) and leakage current ($I_{\text{off}} < 1 \text{ }\mu\text{A}$) specifications (figure 5). These results have allowed defining optimised measurements conditions:

- Drain-Source voltage: $V_{\text{DS}} = 2 \text{ V}$
- Gate-Source voltage: $0 \leq V_{\text{GS}} \leq 2 \text{ V}$

- Drain-Source current: $0 \leq I_{DS} \leq 0.5$ mA

In such conditions, a quasi-Nernstian pH response (sensitivity: 50 - 53 mV/pH) has been obtained after 24 hours stabilisation of the ChemFET microsensor (figure 6).

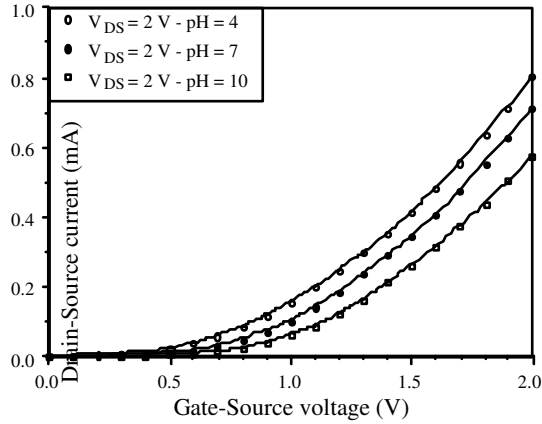


Figure 5. pH-dependent $I_{DS}(V_{GS})$ curves of the FSC-ChemFET microsensor

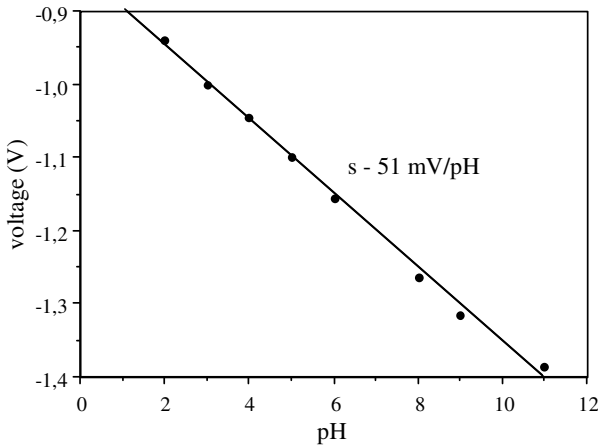


Figure 6. Response of the pH FSC-ChemFET microsensor

Finally, studies concerning the sensor lifetime in water have been performed on a four-month period (figure 7). If the pH sensitivity could be considered as constant, the FSC-ChemFET pH response is characterised by an exponential temporal drift. This phenomenon should be related to interactions between the gate dielectrics and the packaging materials with the aqueous medium. Nevertheless, the temporal drift is lower than its initial maximal value estimated around 3 mV/day. Such results validate the electrical insulation using the P-well technology as well as the packaging process of the FSC-ChemFET microsensors.

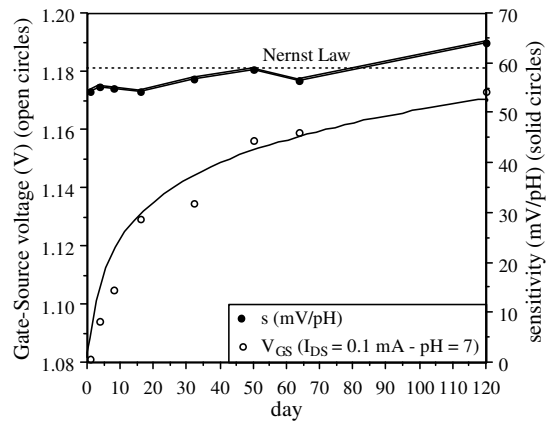


Figure 7. Temporal drift of the FSC-ChemFET microsensor

Adaptation of the FSC-ChemFET microsensors to ions detection

The $\text{SiO}_2/\text{Si}_3\text{N}_4$ front-side connected ChemFET generic microsensors have been extended to ion detection by depositing a polyHEMA layer and an ion-selective siloprene-based membrane on top of the dielectric gate. All in all, the adhesion of the membrane is not very good and the ionosensitive layers can be easily peeled off. Nevertheless, it has been possible to characterise the detection of the NH_4^+ and NO_3^- ions thanks to adapted ionophores.

PNH_4 measurements. A quasi-Nernstian response has been obtained for the detection of the ammonium ion NH_4^+ (figure 8). The sensitivity has been estimated to 50 mV/p NH_4 .

PNO_3 measurements. For the nitrate ion, the results have not been as good as for the ammonium ion since the p NO_3 response is no longer linear for the lowest concentrations. This non-linearity should be related to the selectivity of the ionosensitive membrane. Nevertheless, for the highest concentration, the sensitivity can be estimated around 50 mV/p NO_3 .

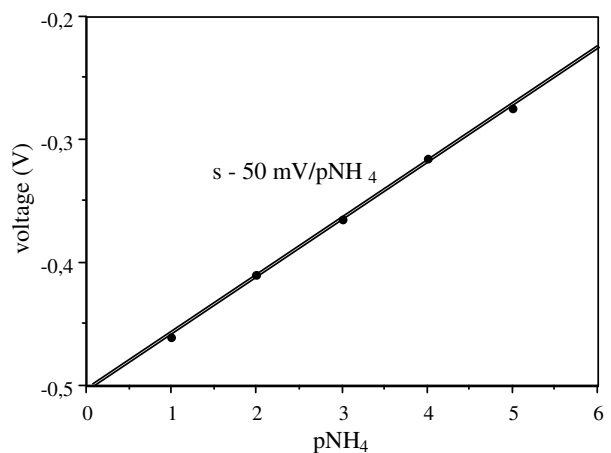


Figure 8. Response of the p NH_4 FSC-ChemFET microsensor

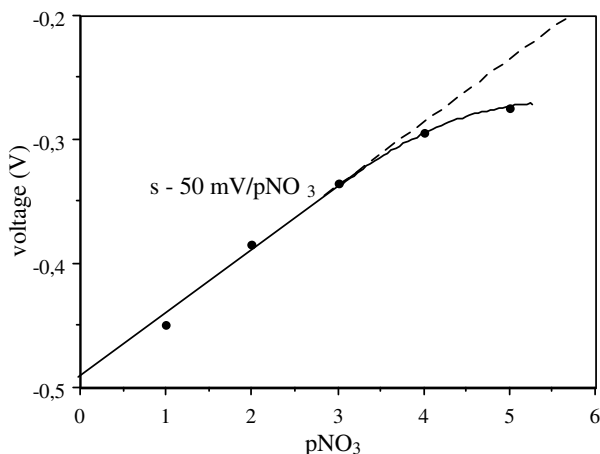


Figure 9. Response of the pNO₃ FSC-ChemFET microsensor

CONCLUSION

SiO₂/Si₃N₄ front-side connected ChemFET generic microsensors have been fabricated taking into account the water analysis requirements and good electrical characteristics have been evidenced through pH measurements. The FSC-ChemFET microsensors have been extended to ion detection by developing a polyHEMA/siloprene-based ionosensitive membrane on top of the dielectric gate. Application has been performed through the NH₄⁺ and NO₃⁻ ions detection, evidencing quasi-Nernstian responses on appropriate concentration ranges.

The front-side connected ChemFETs technology has to be further improved. First, they have to be tested in great number and on longer period in order to characterise more precisely their fabrication yield and their temporal variations (drift, lifetime,...). Such goal will require the understanding of the drift phenomena and the corresponding packaging optimisation. Second, the ionosensitive layers have to be mass-fabricated using PVC-based, siloprene-based and particularly polysiloxane-based membrane. Finally, the ion detection properties have to be studied thoroughly in order to improve their sensitivity and to characterise their selectivity. This RD policy will allow the ChemFETs microsensors improvement in term of reliability and adaptation to the water analysis specifications for their future industrial development.

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REFERENCES

- [1] P. Bergveld, "Thirty years of ISFETology: what happened in the next 30 years and what may happen in the next 30 years", *Sensors and Actuators*, vol. B88, 2003, pp. 1-20
- [2] S. Wakida, M. Yaman, K. Higashi, "Urushi matrix sodium, potassium, calcium and chloride selective field effect transistors", *Sensors and Actuators*, vol. B1, 1990, pp. 412-415
- [3] K. Tsukada, Y. Miyahara, Y. Shibata, H. Miyagi, "An integrated chemical sensor with multiple ion and gas sensors", *Sensors and Actuators*, vol. B2, 1990, pp. 291-295
- [4] A. Errachid, J. Bausells, A. Merlos, J. Esteve, F. Teixidor, C. Perez-Jimenez, J. Casabo, C. Jimenez, J. Bartroli, "Application of simple thioether ionophores to silver ion-selective ChemFETs", *Sensors and Actuators*, vol. B26-27, 1995, pp. 312-324
- [5] M.J. Schöning, M. Sauke, A. Steffen, M. marso, P. Kordos, H. Lüth, F. Kaufmann, R. Erbach, B. Hoffmann, "Ion-sensitive field effect transistors with ultrathin Langmuir-Blodgett membranes", *Sensors and Actuators*, vol. B26-27, 1995, pp. 325-328
- [6] N. Jaffrezic-Renault A. Senillou, C. Martelet, K. Wan, J.M. Chovelon, "ISFET microsensors for the detection of pollutants in liquid media", *Sensors and Actuators*, vol. B59, 1999, pp. 154-164
- [7] J. Sanchez, M. del Valle, "Photocurable ISFET for anionic surfactants - Monitoring of photodegradation processes", *Talanta*, vol. 54, 2001, pp. 893-902
- [8] M. Chudy, W. Wroblewski, A. Dybko, Z. Brzozka, "Multi-ion analysis on versatile sensor head", *Sensors and Actuators*, vol. B78, 2001, pp. 320-325
- [9] Z. Brzozka, M. Dawgul, D. Pijanowska, W. Torbicz, "Durable NH₄⁺-sensitive ChemFET", *Sensors & Actuators*, vol. B44, 1997, pp. 527-531
- [10] E.J.R. Subhölter, 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-sensig membrane interface", *Anal. Chim. Acta.*, vol. 230, 1990, pp. 59-65