

Study of front-side connected chemical field effect transistor for water analysis

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Received 25 August 2003; received in revised form 22 September 2003

Abstract

Front-side connected, N-channel, normally-off, chemical field effect transistor (ChemFET) microsensors including a SiO₂/Si₃N₄ 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 poly-HEMA/siloprene-based ionosensitive membranes. Application is performed through the NH₄⁺ and NO₃⁻ ions detection in artificial solutions, evidencing quasi-Nernstian responses ($s \approx 50$ 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. © 2003 Elsevier Ltd. All rights reserved.

1. 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 fulfill 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⁺, NH₄⁺ and NO₃⁻ ions in aqueous solutions.

2. Experiments

2.1. Sensors technology

Front-side connected (FSC) ion sensitive field effect transistors (ISFETs) were fabricated on (100)-oriented, N-type (500 Ω.cm) silicon substrate. The insulation

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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 (Fig. 1). A 50 nm thermally grown SiO_2 layer and a 50 nm 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 V.

2.2. 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, the polyhydroxyethyl methacrylate (polyHEMA) and the tetrahydrofuran THF used for the fabrication of the ionosensitive layers were also purchased from Fluka.

2.3. 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

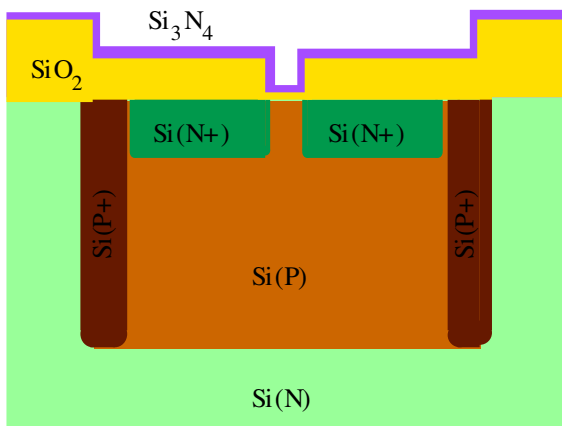


Fig. 1. Cross-section of the front-side connected, P-well, N-channel, ChemFET microsensor.

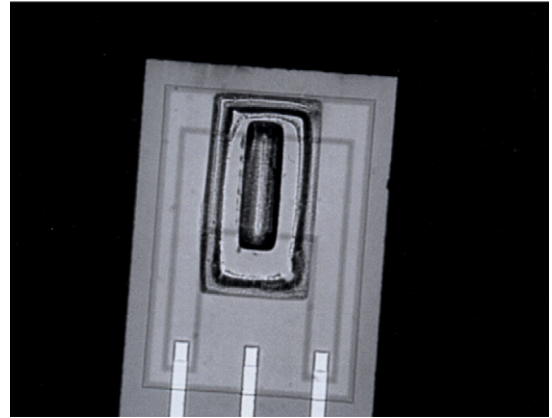


Fig. 2. Photograph of the ChemFET $\text{SiO}_2/\text{Si}_3\text{N}_4$ pH-sensitive gate covered by the polyHEMA membrane and protected by the polysiloxane O-ring.

is the polyHEMA polymer. 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 (Fig. 2) [10]. Finally, the siloprene-based ionosensitive layers were deposited by dip coating on the polyHEMA film [9].

2.4. Sensors packaging

The 2×5 square millimetres ChemFET chips (Fig. 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 (Fig. 2). The packaged FSC-CHEMFETs prototypes are finally represented on Fig. 4.



Fig. 3. Photograph of the FSC-ChemFET silicon chip.

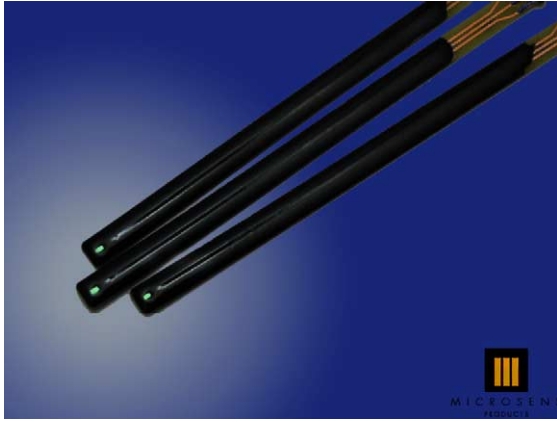


Fig. 4. Photograph of the encapsulated FSC-ChemFET micro-sensor.

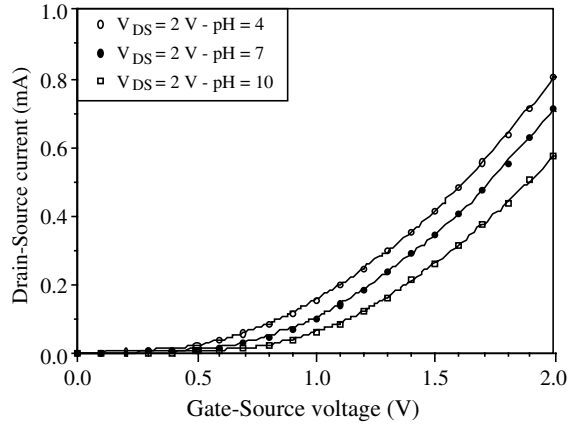


Fig. 5. pH-dependent $I_{DS}(V_{GS})$ curves of the FSC-ChemFET microsensor.

2.5. Measurements

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

3. Results and discussion

3.1. FSC-ChemFET validation through 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 ($V_t < 1$ V) and leakage current ($I_{off} < 1$ μA) specifications (Fig. 5). These results have allowed defining optimised measurements conditions:

- Drain-source voltage: $V_{DS} = 2$ V;
- Gate-source voltage: $0 \leq V_{GS} \leq 2$ 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 h stabilisation of the ChemFET microsensor (Fig. 6).

Finally, studies concerning the sensor lifetime in water have been performed on a four-month period (Fig. 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

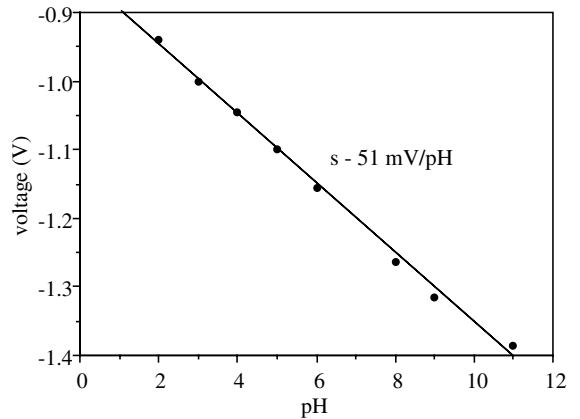


Fig. 6. Response of the pH FSC-ChemFET microsensor.

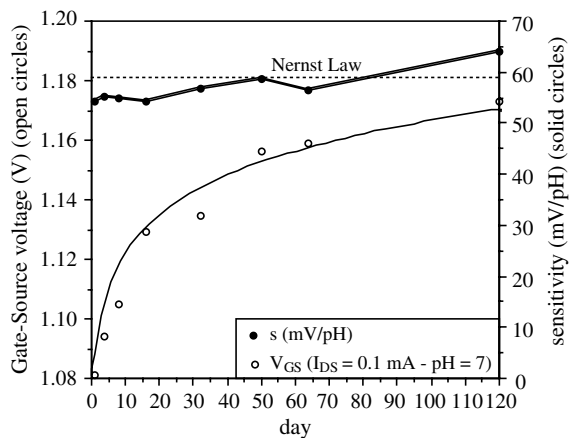


Fig. 7. Temporal drift of the FSC-ChemFET microsensor.

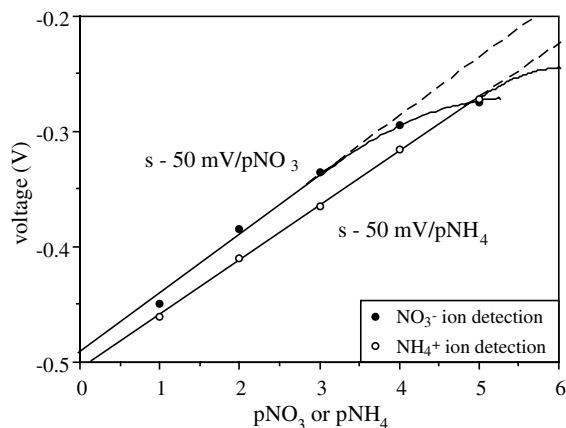


Fig. 8. Responses of the pNH₄ and pNO₃ FSC-ChemFET.

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.

3.2. Adaptation of the FSC-CHEMFETs to ions detection

The SiO₂/Si₃N₄ 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 NH₄⁺ and NO₃⁻ ions thanks to adapted ionophores.

For both ions, results evidence a quasi-Nernstian response for the highest concentrations (sensitivity around 50 mV/pX) and non-linear variations for the lowest concentrations (Fig. 8). This non-linearity should be related to the detection properties of the ionosensitive membrane. Nevertheless, the NH₄⁺ and NO₃⁻ ions detection has been shown on the water analysis appropriate concentration ranges.

4. 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 polyvinyl chloride (PVC) based, siloprene based and particularly polysiloxane (PSX) 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.

Acknowledgements

This work was supported by the European FP5 project "SEWING" (contract no. IST-2000-20084).

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