

Development of pNH_4 -ISFETs microsensors for water analysis

I. Humenyuk, B. Torbiéro, S. Assié, R. Colin, X. Dollat, B. Franc, A. Martinez, P. Temple-Boyer

LAAS-CNRS, 7 avenue du colonel Roche, 31077 Toulouse Cedex 4, FRANCE

Summary: Chemical field effect transistors (ChemFETs) have been fabricated and adapted to the ammonium ion detection thanks to polysiloxane ionosensitive layers. The chip design and packaging process have been optimized to be adapted to a specific flow head measurement system. Experimental results evidence quasi-nernstian response for the pNH_4 measurement. This microsensor will be used for water analysis applications.

Keywords: Chemical field effect transistor, ammonium detection, water analysis

Introduction

The water analysis techniques require the development of smart chemical sensors with the following properties: mass fabrication, low cost, low power and ease of use. In this goal, the chemical field effect transistor (ChemFET) is a serious candidate. Indeed, it provides all the requested advantages and its potentiometric principle is well adapted to the detection of ions [1]. Thus, many polymer-based ionosensitive layers have been used for the development of ion-sensitive field effect transistors (ISFETs) [2, 3]. To go further, the ISFETs microsensors have to be adapted to the water analysis specifications. This requires the improvement of the whole ISFET fabrication and measurement procedures, including chip design, technological process, ionosensitive layers integration, packaging process, measurement system and data treatment.

This paper deals with such development of front-side connected (FSC) ChemFETs for water analysis applications, and more especially for the detection of the NH_4^+ ion in aqueous solutions.

Experimental

Front-side connected (FSC), N-channel, normally off, $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate, pH -ChemFETs were fabricated using standard P-well technology [4]. The silicon chip also includes a reference metal oxide silicon field effect transistor (ReMOS) for drift or temperature compensations (figure 1).

The pH -ChemFETs were adapted to the NH_4^+ ion detection using the polysiloxane (PSX) copolymer RMS-033 (purchased from ABCR). The PSX membranes were prepared according to a technological process developed by the Warsaw University of Technology [2]. It contained 100 mg of polysiloxane (PSX), 10 mg of 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator, 1 mg of nonactine acting as ammonium-sensitive ionophore and 2 ml of tetrahydrofuran (THF) used as solvent. After the THF evaporation at 80°C (duration: 6 hours) and the 3-(methacryloxy)propyl

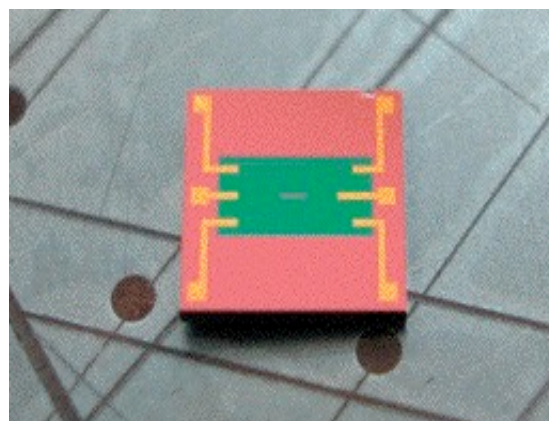


Fig. 1. Photograph of the $5 \times 5 \text{ mm}^2$ pH -ChemFET/ReMOS silicon chip

trimethoxysilane (MPTS) / toluene silanisation step at 80°C to promote adherence, the membrane solution (approximately $10 \mu\text{L}$) were deposited by dip coating on the $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate (PSX thickness: $10 \mu\text{m}$). Then, the PSX membranes photopolymerization was obtained by exposure to UV (duration: 200 s, illumination power: 20 mW) under a non-oxidizing ambient. All the chemical reagents required by this technological process were purchased from Sigma-Aldrich.

Finally, the $5 \times 5 \text{ mm}^2$ FSC, pNH_4 -ChemFETs chips were reported on $9 \times 9 \text{ mm}^2$, back-side-connected printed circuit boards (BSC-PCB). After gold wedge wire bonding, they were encapsulated using two different epoxy resins (H70E-4 and H70E-2 purchased from Epoxy Technology). A two-step dispense process was developed to leave the $\text{SiO}_2/\text{Si}_3\text{N}_4/\text{PSX}$ ionosensitive gate uncovered (figure 2).

The whole ChemFET microsensor, i.e. the FSC-ChemFET chip and the BSC-PCB, as well as the packaging process were studied in order to be compatible with the flow-through head concept developed by the Warsaw University of Technology [5]. A specific characterization stand was finally developed in order to prepare and supply continuously liquid samples. It regroups different fluidic equipments (liquid distribution

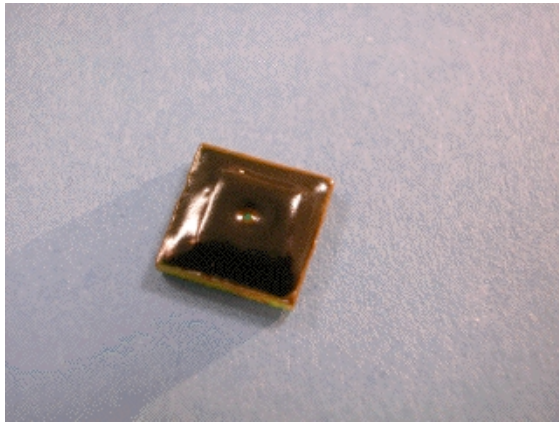


Fig. 2. Photograph of the pNH_4 -ISFET back-side connected microsensor

system, cooling/heating stirrer, peristaltic pump, liquid flow controller, pneumatic valves), the flow-through head (including the reference electrode) and a ChemFET measurement interface also called ChemFETmeter. All the characterization system was monitored by a personal computer for data acquisition and control. Thus, thanks to this characterization stand, the pNH_4 -ChemFET-properties were studied for various ammonium-based solutions ($1 \leq \text{pNH}_4 \leq 5$), all the measurements being carried out at room temperature.

Results and discussion

Firstly, the H^+ ion detection properties of the pNH_4 -ISFETs have been studied. No detection properties have been found, showing that the pH-sensitive $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate structure is no longer active.

Thus, the ammonium NH_4^+ detection properties have been studied after keeping the microsensors in a conditional NH_4NO_3 (10^{-1} M) solution for a day. Figure 3 shows a typical response time for pNH_4 ranging from 1 to 5.

Thanks to these data, the responses curves of the pNH_4 -ISFETs sensors based on the dip-coated ionosensitive layers have been studied. Thus, even if saturation phenomena are evidenced for the lowest concentrations, quasi-nernstian sensitivity, i.e. around 45 mV/pNH_4 , have been evidenced on the water analysis appropriate concentration ranges ($1 \leq \text{pNH}_4 \leq 4$).

Nevertheless, results must be balanced by the use of dip-coated PSX ionosensitive layers. Indeed, such process is not compatible with the chemical sensors industrial fabrication. To do so, mass-fabrication processes have to be developed using standard spin coating and photolithography techniques. Such policy will lead to the fabrication of pNH_4 -ISFETs sensors based on the spin-coated ionosensitive layers. Thus, the ammonium NH_4^+ ion detection properties of such sensors will be studied and compared to standard one in further works.

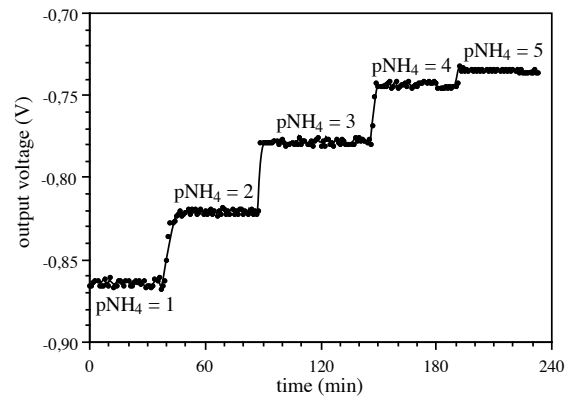


Fig. 3. Response curves of the pNH_4 -ISFET sensor based on dip-coated PSX ionosensitive layers

Conclusion

$\text{SiO}_2/\text{Si}_3\text{N}_4$ front-side connected ChemFET generic microsensors have been fabricated, adapted to ion detection thanks to a polysiloxane-based (PSX) ionosensitive membrane deposited by dip coating on top of the dielectric gate, and reported on back-side connected printed circuit board to fit to the water analysis specifications. Application has been performed through the ammonium NH_4^+ ion detection, evidencing quasi-nernstian responses on appropriate concentration ranges ($1 \leq \text{pNH}_4 \leq 5$). Further developments will present results obtained thanks to ammonium sensitive PSX layers mass-fabricated using spin coating and photolithography techniques.

Acknowledgements

This work was supported by the European FP5 project "SEWING" (contract n° IST-2000-20084).

References

1. P. Bergveld; *Sensors & Actuators*, B88 (2003), pp 1-20.
2. W. Wroblewski, M. Chudy, A. Dybko, Z. Brzozka; *Analytica Chimica Acta*, 401 (1999), pp 105-110.
3. M. L Hamlaoui, R. Kherrat, M. Marrakchi, N. Jaffrezic-Renault, A. Walcarius; *Materials Science and Engineering*, C21 (2002), pp. 25-28.
4. P. Temple-Boyer, J. Launay, I. Humenyuk, T. Do Conto, A. Martinez, C. Bériet, A. Grisel; *Microelectronics Reliability*, 44 (2004), pp. 443-447
5. M. Chudy, W. Wroblewski, A. Dybko, Z. Brzozka; *Sensors & Actuators*, B78 (2001), pp. 320-325.