

DEVELOPMENT OF PNH_4^+ SENSITIVE ISFET

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Front-side connected, N-channel, normally-off, $\text{SiO}_2/\text{Si}_3\text{N}_4$ Ion Sensitive Field Effect Transistor (ISFET) microsensors have been fabricated and adapted to the ammonium ion detection thanks to polysiloxane ionosensitive layer. This photosensitive polymer has been deposited on dielectric gate and patterned either by dip coating, either by spin coating and photolithography techniques. The sensitivity characteristics of both structures have been studied. The sensors have been shows a good quasi-nernstian sensitivities to NH_4^+ cation in the different solution of ammonium nitrate (NH_4NO_3) [10^{-5} ... 10^{-1}] M

Introduction

The measurement principle for ion concentration of chemical solution based on field-effect transistor with insulated gate was proposed in 1970 by Bergveld [1]. The Ion-Sensitive Field Effect Transistor (ISFET) has been derived from microelectronics and has the following properties: small size, compatible with mass fabrication, low cost, low power and generic function. ISFET actively have been developed for several applications (blood, water analyses...). Ion-selective membrane operates as under-gate dielectric in measured ISFET and tested medium (electrolyte) with reference electrode work as gate. Moreover, in contrast to ion-selective electrode, membrane is any material which has interfacial potential dielectric gate/solution. Informative parameter of chemical sensor ISFET is threshold voltage which changes at variation of ion concentration in tested solution. The main preference of such chemical sensors is their full compatibility with integrated circuit technology. The ISFET thanks to these properties are taking an increasing place in the market of chemical microsensors more precisely in the domain of water analysis. While pH-ISFET has been developed successfully using well known sensitive layers (Si_3N_4 , Ta_2O_5 , Al_2O_3) a suitable sensitive membrane for NH_4 ion detection needs more investigation. Several tests have been done to find an optimal matrix for ionophore [2]. The layers based on polysiloxane (PSX) show good adhesion properties and are suitable for the preparation of ion sensitive membranes.

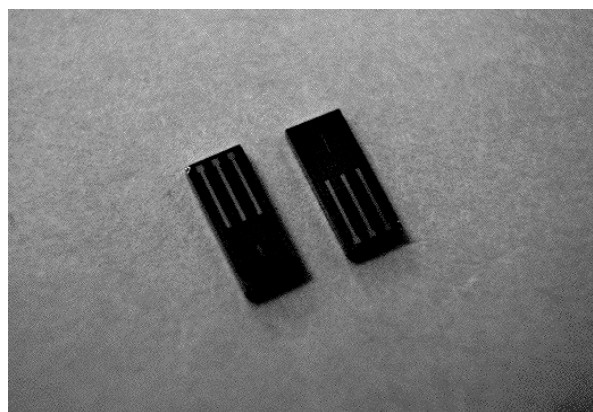
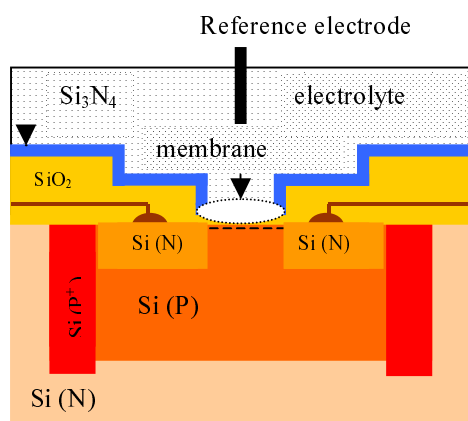
This paper deals with such development of front-side connected FSC-ChemFETs microsensors for water analysis. It presents the global improvement of the fabrication procedure, taking into account the chip design, the technological process, and the deposition of polysiloxane-based ionosensitive layers. The results have been obtained through NH_4^+ ion detection in aqueous solutions.

Experimental

Front-side connected (FSC) Ion Sensitive Field Effect Transistors (ISFETs) were fabricated on $\langle 100 \rangle$ -oriented, N-type ($500 \Omega \cdot \text{cm}$) 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 (Fig. 1a). A 50nm thermally grown SiO_2 layer and a 100nm Si_3N_4 layer deposited on top formed the pH-sensitive gate structure. 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.

The 2×5 square millimetres ChemFET chips (Fig. 1b) were reported on a specific printed circuit board and encapsulated with silicon glue leaving uncovered gate insulator.

The pH-ISFETs were adapted to the NH_4^+ ion detection using polysiloxane-based ionosensitive layers. The PSX layers were deposited on the pH-sensitive gate ($\text{SiO}_2/\text{Si}_3\text{N}_4$) either by dip-coating, either by spin-coating and photolithography techniques [3].



a

b

Fig. 1. a) section of the front-side connected, P-well, N channel, ChemFET microsensor
b) photograph of the pH-ISFET SiO₂/Si₃N₄, fabricated in LAAS-CNRS, France

The PSX membranes were prepared for dip coating [4]. It contained 50 mg of polysiloxane (PSX), 0.5 mg of 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator, 1 mg of nonactine acting as ammonium-sensitive ionophore, 0.6 mg of lipophilic salt KTFPB and 0.5 ml of tetrahydrofuran (THF) used as solvent. After the THF evaporation at 80°C (duration: 6 hours) and the 3-(methacryloxy)propyl trimethoxysilane (MPTS) / toluene silanization step at 80°C to promote adherence.

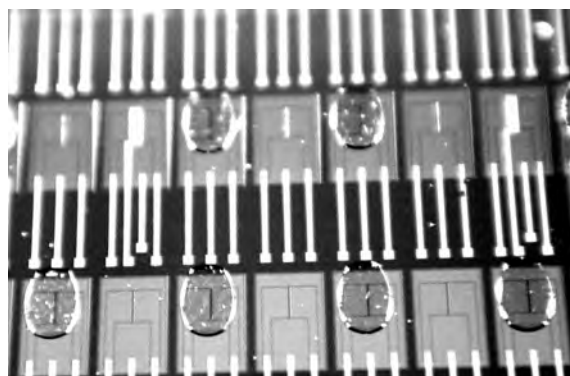
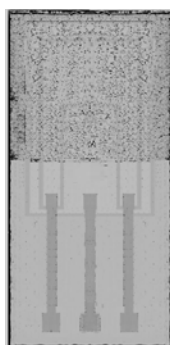


Fig. 2. Photo of NH₄⁺ sensor with dip coating deposited membrane

Fig. 3. Photo of NH₄⁺ sensors with spin coating deposited membrane

A droplet of PSX membrane solution (approximately 8 μL) was deposited by a micropipette on the dielectric gate SiO₂/Si₃N₄. Then, the PSX layers (thickness around 10 μm) photo-polymerization was obtained by exposure to ultraviolet (UV) illumination (duration: 200 s, power: 20 mW) under a non-oxidizing ambient (fig. 2).

The mass-fabrication process of polysiloxane thin layers by spin coating and ultraviolet photolithography techniques has been adapted from the previous one. The mixture for photosensitive polymer contained: 1% of ammonium ionophore, 1% of DMPA and 0.6% of lipophilic salt KTFPB related to weight of polysiloxane RMS-033. The membrane components were dissolved in THF.

After a MPTS/toluene silanization step at 80°C to promote adherence on the silicon substrate, the PSX-based solution was deposited by spin-coating using a SUSS GYRSET RC-8 spin coater. Then, after the THF solvent evaporation under nitrogen atmosphere, ultraviolet (UV) exposure was performed under a non-oxidising ambient using a Karl Suss MA-6 contact alignment system. Finally, the PSX patterns were obtained using xylene as developer (fig.3). The thickness of PSX layers obtained by spin coating is 45 μm. Ultraviolet diffraction phenomena are still responsible for the fabrication of badly defined PSX layers and the whole spin-coating and photolithography process has still to be improved. Nevertheless, these technological results show the feasibility of mass-fabricated, PSX-based, pNH₄-ISFETs.

Result and discussion

Characterization of both structures was done using analyzer HP4140B.

The gate-source voltage has been applied to the solution versus a pseudo reference electrode. Gold wire has been used as metallic gate. The ISFETs chemical sensors with dip coating deposited membrane were characterised by I-V experiment at constant drain-source current $I_{DS} = 0.1\text{mA}$ and drain-source voltage $V_{DS} = 1\text{V}$, the P-well being connected to the source and the substrate being not connected. The test of ISFETs sensors with mass fabricated membrane was done at constant drain-source current $I_{DS} = 20\ \mu\text{A}$ and drain-source voltage $V_{DS} = 3\ \text{V}$. All the measurements were carried out at room temperature and illumination.

Finally, after keeping the pNH_4 -ISFET microsensors in a conditional NH_4NO_3 ($10^{-1}\ \text{M}$) solution for a 48h their detection properties were studied for various ammonium-based solutions ($1 \leq \text{pNH}_4 \leq 5$).

Firstly, the H^+ ion detection properties of the pNH_4 microsensors have been studied. If quasi-ernstian pH sensitivity was evidenced for the former pH-ISFETs [5], no detection properties have been found for the pNH_4 -ISFETs whatever the PSX-based ionosensitive layers deposition techniques.

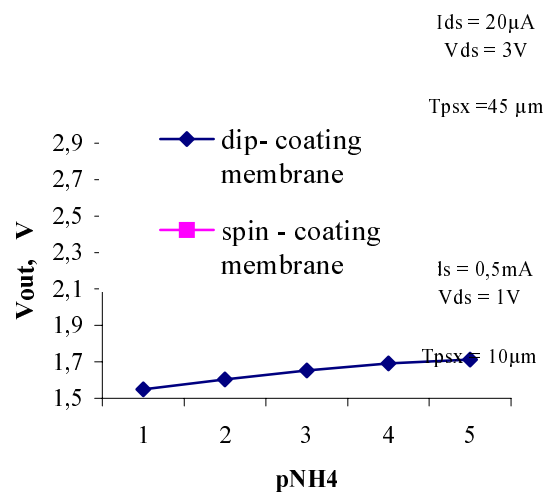


Fig. 4. Sensitivity of pNH_4 sensor with dip-coating membrane

This result shows that the pH-sensitive $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate structure is no longer active after the polysiloxane layers deposition (figure 4).

Thus, the ammonium NH_4^+ ion detection properties have been studied. Figure 4 shows a typical response obtained for the dip-coated, ionosensitive, polysiloxane layers. Even if saturation phenomena are evidenced for the lowest concentrations $\text{pNH}_4 \approx 5$, quasi-ernstian sensitivity, i.e. around $48\ \text{mV}/\text{pNH}_4$, have been evidenced on ammonium NH_4^+ ion concentration ranges ($1 \leq \text{pNH}_4 \leq 4$) appropriate with the water analysis. Nevertheless, different drawbacks of the dip-coating process have been highlighted. First, it is responsible for positioning problems of the PSX ionosensitive layers onto the $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate. Second, it is characterised by the non-reproducibility of the deposited PSX droplets, preventing from obtaining a good measurement reproducibility of the pNH_4 -ISFETs. As a result, the mass-fabrication process using spin-coating and ultraviolet photolithography techniques has been developed.

Doing the same I (V) characterization of NH_4 sensors with mass membrane fabrication the important shift of threshold voltage has been remarked. The thickness of PSX sensitive layer will affect the capacitance capability and surface site density of the membrane lead to increase of the threshold voltage and decrease of the drain current.

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.

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SENSIVITY AND AVERAGE TEMPERATURE OF LATGS PYROELECTRIC DETECTOR

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New obtained single crystal LATGS and its selected dielectric properties are presented in this paper. Samples of the single crystal were utilised as active elements of pyroelectric detector. This paper contains also theoretical considerations for this type of detector, making possible determination of voltage-current sensitivity.

1. Introduction

Pyroelectric detectors which found applications in contemporary electronics. This kind of detection devices do not need cooling, which is one of the greatest disadvantages of detectors based on semiconductors. Pyroelectric detectors can operate in wide range of radiation spectra. Pyroelectric materials are in most cases ferroelectrics, based on ceramics or single crystals. One of the groups of materials being used in fabrication of pyroelectric detectors are single crystals, with second order ferroelectric phase transition. Triglycine Sulphate single crystals doped with L- α -alanine (LATGS) belong to this group of ferroelectrics.

Researches presented in the paper contain selected results of dielectric parameters investigation, necessary to establish sensitivity of the detector.

2. Experiment

Single crystals were grown from water solution containing glycine and sulphuric acid in stoichiometric ratio. Such obtained solution was mixed with L- α - alanine with concentration of 10%. Growth temperature was stabilised at 300 K. Obtained single crystals poses ferroelectric properties in (010) direction.