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New fluoride-sensitive membranes prepared through an ion implantation process

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A new technique used in order to realize fluoride ion-sensitive membranes is presented. This method consists of the ion implantation technique which is highly compatible with integrated circuit (i.c.) technology. This technique can be used for realizing various inorganic membranes for sensing purposes.

In this paper, we studied two thin film membranes based on lanthanum and calcium fluoride compounds for fluoride detection, through the ion implantation technique. The electrical and chemical properties of the films obtained are studied on electrolyte/oxide/semiconductor structures (EOS). The fluoride ion sensitivity is determined using capacitance voltage measurements for the EOS structures. The response obtained is 44 mV per decade in the range of pF^- 4 to 2 for LaF_3 membrane, and 52 mV per decade in the range of pF^- 3 to 1 for CaF_2 membranes. Finally, we present data for fluoride sensitive ISFET (ion sensitive field effect transistor) microsensors using the developed CaF_2 membrane with a corresponding REFET (reference field effect transistor) in individual and differential mode.

1. Introduction

In 1970, Bergveld introduced the first ion-sensitive field effect transistor (ISFET) [1]. Chemical microsensors based on the field effect transistor (FET) have induced a lot of research because of their specific advantages such as low cost, small size and robustness. Moreover, one of their most attractive fields, where their potential could give valuable results, is biomedical engineering, specially for *in vivo* monitoring of pH or other ion concentrations such as sodium. pH-FETs are commercially available, mainly for environmental applications such as water or soil control, laboratory purposes, food control such as meat or fish freshness. As has been written recently [2] they are expected to be followed soon by CHEMFETs (chemically modified field effect transistors). For fluoride detection, sensitive membranes can be obtained either by pressing a thermoplastic mixture of tetrafluoroethylene and LaF_3/5% BF_2 [3] or by radio frequency deposition of LaF_3 films [4]. These techniques permit the deposition of a thick fluoride membrane (over 1 μm), and are not usually compatible with standard silicon technology process (i.c. technology) or can be considered very dangerous because of the properties of lanthanum (lanthanum is inflammable in air). In spite of these drawbacks, an alternative based on preparing the F^- sensitive membrane by the ion implantation technique is investigated. This technique can be considered as more promising, thanks to its compatibility with i.c. technology and the possibility of obtaining a thin sensitive membrane (lower than 50 nm thick) within the insulator film of FET devices.

The ion implantation approach was first explored by Sanada *et al.* [5], who implanted lithium ions at 50 keV and aluminium ions at 60 keV in a plasma SiN layer deposited on the ISFET silica insulator. More detailed investigations were performed in order to detect sodium [6, 7] and potassium ions [8]. The sensitive membrane obtained presents a high sensitivity, selectivity and a long life time (the sensitivity of the sensor remain unchanged even after 1 year).

In connection with research on such a new technique permitting the fabrication of various sensitive membranes, we present the feasibility of high fluoride sensitive membranes (LaF_3 and CaF_2) for microsensors by implanting ions, in mild conditions, into a thin layer of insulator.

2. Experimental procedure

2.1. Electrolyte/oxide semiconductor (EOS)

The sample was a [1 0 0] *p*-type silicon wafer with 3–5 Ω cm resistivity and 400 μm thickness, cut into 10 × 10 mm pieces. The insulator layer was thermally

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grown (100 ± 5) nm thick SiO_2. The ohmic contact on the silicon back side was obtained by overdoping it with boron ions.

2.2. ISFET fabrication

The ISFETs used were *N*-channel depletion mode microdevices produced using the facilities of CIME (Grenoble, France). They were formed on a chip designed with a specific geometry (1.2 mm wide, 12 mm long and 300 μm thick), the dimensions of the channel being 20 μm long and 500 μm wide. The gate insulator was a thermally grown SiO_2 layer 100 nm thick [9]. The ISFET chip was encapsulated in an epoxy resin except for the sensitive area.

2.3. Preparation of F^- sensitive membranes

The LaF_3 membranes were obtained by implanting fluoride and lanthanum ions into the silica insulator of the transducer (EOS or ISFET). The ion implantation conditions (fluence and energy) were theoretically calculated [10] in order to match the microsensor (ISFET and EOS structure) characteristics described above. The profile presented in Fig. 1 is calculated in order to obtain 20% by atomic composition of LaF_3 and 50 nm of the total implanted layer. The corresponding fluences and accelerating energies of the implanted ions were 2×10^{16} ions cm^{-2} at 30 keV for lanthanum and 5×10^{16} ions cm^{-2} at 10 keV for fluoride. After implantation, the sample was annealed at 200 °C for 10 min under nitrogen atmosphere.

Furthermore, we studied CaF_2 membranes, for fluoride ion detection, by implanting calcium with a fluence of 10^{16} ions cm^{-2} at 25 keV accelerating energy and fluoride ions with a fluence of 2×10^{16} ions cm^{-2} at 12 keV. As shown in Fig. 2, the obtained layer is composed of 5% Ca, 22% F in the SiO_2 which corresponds to a composition of 5% CaF_2, the depth of the obtained CaF_2 membrane was about 60 nm. A thermal treatment at 400 °C for 20 min under nitrogen atmosphere was used to reduce damage induced during the implantation process.

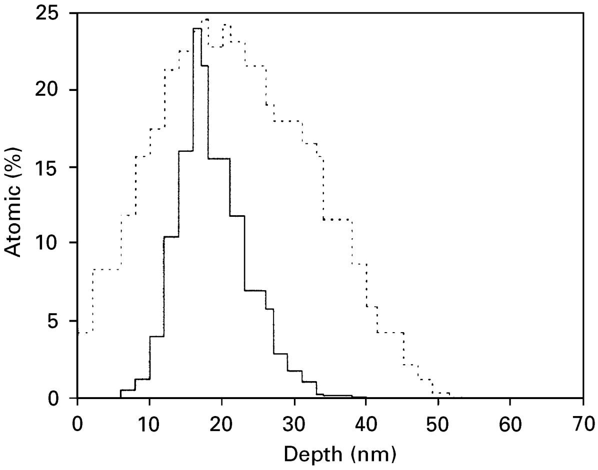

Figure 1 The implanted profile of fluoride (– – –) and lanthanum (——) ions within the silica ($D_F = 5 \times 10^{16}$ $^{19}F\,cm^{-2}$ $E_F = 10$ keV; $D_{La} = 2 \times 10^{16}$ $^{139}La\,cm^{-2}$ at $E_{La} = 25$ keV).

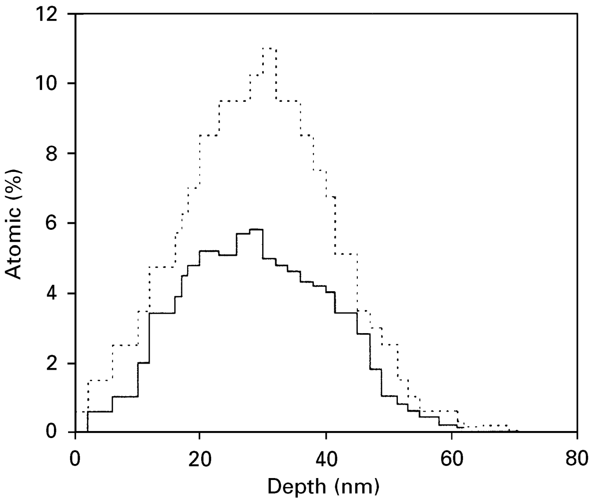

Figure 2 The implanted profile of calcium (——) and fluoride (– – –) ions ($D_{Ca} = 10^{16}$ $^{40}Ca\,cm^{-2}$ at $E_{Ca} = 25$ keV; $D_F = 2 \times 10^{16}$ $^{19}F\,cm^{-2}$ $E_F = 12$ keV).

The reference field effect transistor (REFET) membranes were obtained by implanting at the same accelerating energy, while the fluences of the implanted ions were 1/100 lower than for corresponding sensitive layers.

2.4. Electrical characterization and test solutions

The EOS structures were characterized by impedance measurements and specially by the capacitance-voltage method [11]. All measurements were performed in an electrochemical cell with three electrodes [12]: the sample, Pt electrode, and saturated calomel electrode (SCE) or platinum electrode for measuring the response of the chloride interfering ion. The d.c. bias and a superimposed alternating signal were applied to the sample and measured versus the SCE. The amplitude of the alternating signal was 10 mV r.m.s. at 10 kHz frequency.

The ISFET and ISFET/REFET type microsensors were characterized using, respectively, individual and differential modes with amplifiers working in a classical source follower configuration.

The solutions used for testing the ion sensitivity were 2% tris(hydroxymethyl)-aminomethane solutions in bidistilled water, at a fixed pH value of 7.2: a constant ionic strength was maintained at 0.4 M of KNO_3. KF and $CaNO_3$ of analytical grade were added in a concentration range of 10^{-4} M to 10^{-1} M.

All the measurements were carried out in the dark and in thermostatic room temperature.

3. Results

The sensitivity of the obtained LaF_3 and CaF_2 membranes obtained by ion implantation, were first studied by using the C(V) response of the EOS structure. We have also studied the ability for these membranes to be used as ISFET membranes. Their sensitivities, selectivities and response times were studied in individual and differential modes of ISFET/REFET devices.

3.1. LaF_3 membranes

The surface state density of the implanted EOS structure increased during the ion implantation process. In fact, Fig. 3 shows a typical C(V) curve of an EOS structure presenting a high surface state density, the C(V) curve was asymmetric and the V_{FB} value was higher than 3 V, implying that the surface state density is about 7.5×10^{11} ions cm^{-2}. This surface state contamination is due to the sputtering of the surface effect and the diffusion of fluoride ions during lanthanum implantation. Fig. 4 shows that the sensitivity of the obtained LaF_3 membrane is 44 mV per decade in the 10^{-4} to 10^{-2} M range. However, it was insensitive to interfering chloride ions.

In order to determine the response time of the LaF_3 membrane, we reported the experimental conditions of the ion implantation and annealing treatment for an ISFET microsensor. Nevertheless, the implanted ISFET cannot be tested and no field effect is obtained.

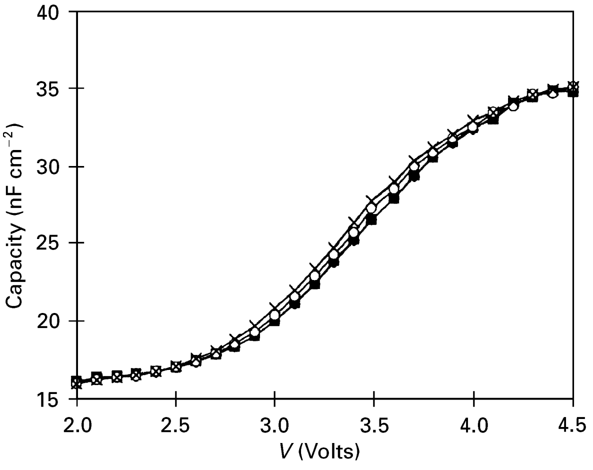

Figure 3 The C(V) curve for varied concentrations of fluoride solution ($D_F = 5 \times 10^{16}$ ^{19}F cm^{-2} $E_F = 10$ keV; $D_{La} = 2 \times 10^{16}$ ^{139}La cm^{-2} at $E_{La} = 25$ keV). pF = (◆) 5, (■) 4, (○) 3, (×) 2 and (—) 1.

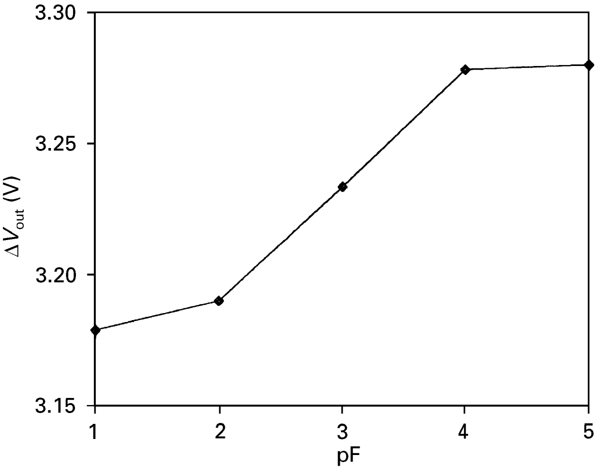

Figure 4 The response of the LaF_3 membrane versus fluoride concentrations ($D_F = 5 \times 10^{16}$ ^{19}F cm^{-2} $E_F = 10$ keV; $D_{La} = 2 \times 10^{16}$ ^{139}La cm^{-2} at $E_{La} = 25$ keV).

Due to the difficulty in obtaining an LaF_3 sensitive membrane for an ISFET sensor by the ion implantation technique, without short circuiting the drain source and without increasing the surface state density, we studied the calcium fluoride membrane.

3.2. CaF_2 sensitive membrane

As a basis of our analysis, we first studied the C(V) response of a CaF_2 membrane for an EOS structure. Fig. 5 shows a typical shift of the flat-band voltage ΔV_{FB} versus fluoride concentration. The sensitivity obtained for fluoride ions is Nernstian in the range of 10^{-3} to 10^{-1} M. However, as shown in Fig. 6, the CaF_2 membrane is sensitive to calcium and chloride interfering ions. For calcium, the response obtained for a high concentration is about 2 mV, whereas the response obtained for chloride ions varies from 5 to 20 mV per decade. The F^- selectivity is quantified by

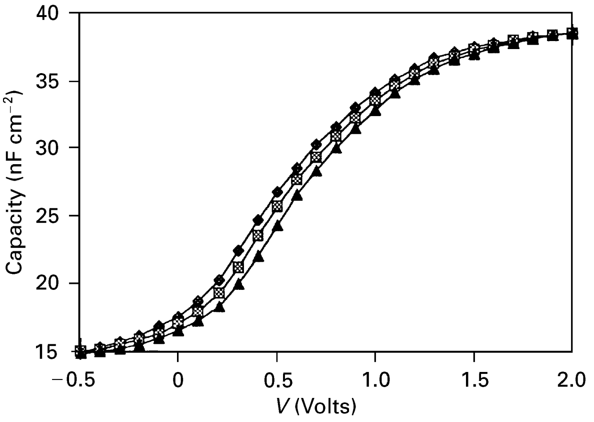

Figure 5 C(V) shift versus fluoride ions. pF = (◆) 1, (■) 2, (▲) 3.

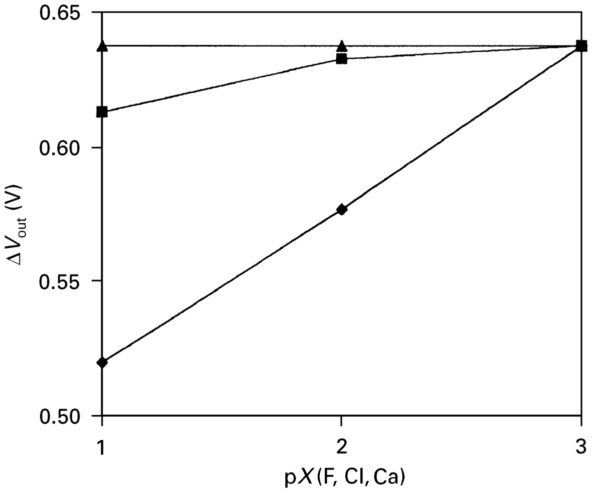

Figure 6 The response of CaF_2 membrane versus fluoride (◆), chloride (■) and calcium (▲) ions.

means of a selectivity coefficient given by Eisenman's equation

$$V_{\mathrm{FB}} = V_{\mathrm{FBi}} - \frac{RT}{F}\ln(a_{\mathrm{F}} + K^{\mathrm{pot}}_{F_{\mathrm{i}}} a_{\mathrm{i}}^{1/Z_{\mathrm{i}}})$$

where a_{F} is the concentration of F^-, a_{i} and Z_{i} are the concentration and the charge of the interfering ion i, R is the gas constant, T is the temperature in Kelvin, F is the Faraday constant, and V_{FBi} is the initial flat band voltage. By using the "separate solution" technique [13], the selectivity coefficient of the chloride and calcium can be calculated. The values obtained are $K^{\mathrm{pot}}_{\mathrm{FCa}} = 10^{-2}$ and $K^{\mathrm{pot}}_{\mathrm{FCl}} = 2 \times 10^{-2}$.

As for the $\mathrm{LaF_3}$ membrane, we have studied the feasibility and the response obtained with an F^- ISFET based on a $\mathrm{CaF_2}$ sensitive membrane. As shown in Fig. 7, the response obtained in the individual mode is quasi-Nernstian in a range of 10^{-3} to 10^{-1} M and the detection limit is about 10^{-4} M. The typical kinetic response of the ISFET obtained by ion implantation is shown in Fig. 8. The major part of the response is reached within 1 s, and the total response is achieved in less than 30 s. The response to the interfering ions was similar to that obtained for the EOS structure. However, the response time of the ISFET for chloride response is higher than for fluoride ions (see Fig. 9), the total response is achieved in 21 min for 10^{-2} M chloride concentration and in 1 min for a higher concentration. These microsensors show a high drift of about 40 mV h^{-1}.

Its corresponding REFET is prepared in the same accelerating energies and annealing conditions as for the ISFET. Only the fluence of the implanted ions was modified: it was 100 times lower than for the ISFET membrane. The obtained REFET presents a small response (higher than 2 mV) for a high concentration (lower than 0.1 M) of fluoride and chloride ions. These responses were probably due to the change of the ionic strength. The drift of the REFET is about 37–38 mV h^{-1}.

Finally, as shown in Fig. 10, the measurements obtained in differential mode (ISFET/REFET devices) were similar to the individual mode, only the drift was reduced. It was about 1 mV h^{-1} in differential mode.

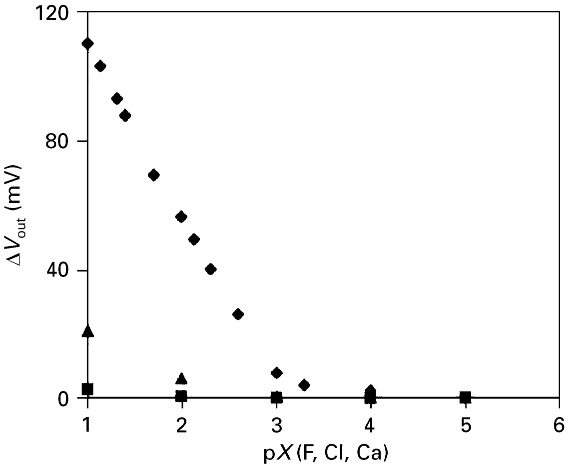

Figure 7 The response of the implanted F^--ISFET, versus fluoride (◆), chloride (▲) and calcium (■) concentrations.

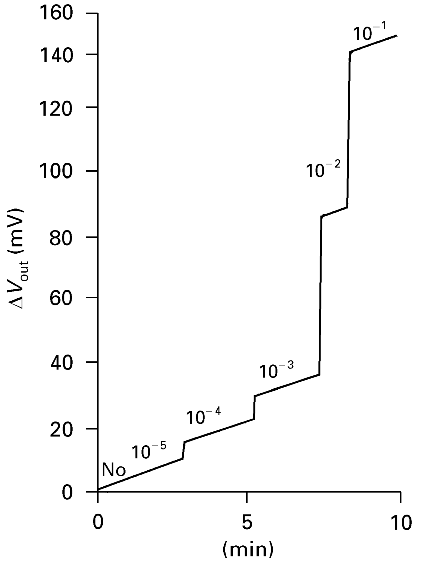

Figure 8 The kinetic F^--ISFET response for successive fluoride additions.

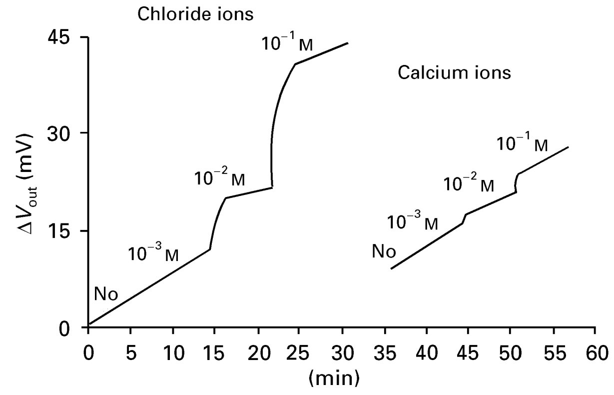

Figure 9 The kinetic F^--ISFET response for the interfering ions.

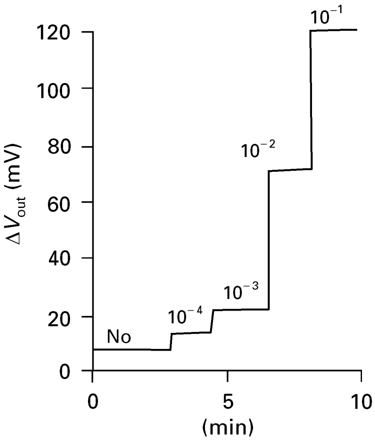

Figure 10 Kinetics of fluoride sensor in differential mode for successive fluoride additions.

The differential mode also allows a reduction of external parameters such as pH, light and temperature which have a similar influence on each individual microdevice.

4. Conclusions

The feasibility of fabricating of F^- sensitive membranes by implanting ions in mild conditions into the insulator layer of the ISFET device has been experimentally proved. The ion implantation technique permits the obtention of a sensitive layer in the transducing part itself, with high sensitivity and selectivity. However, we have remarked that it is suitable for implanting ions whose atomic weight is comparable (short average weight between the two implanted ions). In addition, the implantation of heavy ions is not suitable because the process irreversibly damages the sensor. Ion implantation appears to be a common technique which is fully compatible with i.c. technology, for functionalizing the insulator layer of microsensors, varying the sensitive membrane of the ISFET and its corresponding REFET. So ion implantation can be considered as a very promising technique for the fabrication of inorganic membrane ISFETs, especially in the design of multimicrosensors.

For the environmental field, such microsensors are of great interest for continuous monitoring for environment control. In the case of fluoride determination in polluting soil, the F^- ISFET/REFET system is well suited.

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