

Development of REFET for Differential Measurements of pH in a Fluidic System

Abstract. This paper describes the fabrication of the REFET structure by means of plasma oxidation of silicon nitride and discusses the results of differential pH measurements and quasi-REFET characterization. The source follower measurement circuit and housings for the fluidic systems are shown. The pH measurement of the diluted hydrochloric acid is presented as an exemplary application.

Streszczenie. W pracy przedstawiono dotychczasowy rozwój technologii REFETów. Opisano wytwarzanie REFETa metodą utleniania plazmowego warstwy azotkowej. Zaprezentowano układ pomiarowy wtórnika źródłowego i obudowy przepływowe. Podano wyniki kwalifikacji kwazi-REFETów i różnicowych pomiarów pH. Zaproponowano zastosowanie przyrządu wraz z pseudoreferencyjną elektrodą Pt do pomiarów w rozcieńczonym HCl.
Rozwój technologii REFETów z przeznaczeniem do pomiaru pH

Keywords: REFET, ISFET, Reference electrode.

Słowa kluczowe: REFET, ISFET, elektroda referencyjna.

doi:10.12915/pe.2014.11.39

Introduction

Ion Sensitive Field Effect Transistors (ISFET) are used as a versatile basic devices for fabrication of various chemical and biochemical sensors. According to this concept a liquid analyte is used as a gate electrode of the transistor. Analyte potential is controlled by means of a reference electrode. The Ag/AgCl reference electrode exhibits stability in a water solution of chloride ions when the concentration is kept constant. The electrode is usually placed in a tube filled with KCl solution and separated from the analyte by a porous membrane. This arrangement of the reference electrode makes miniaturization hardly possible.

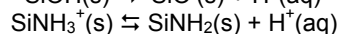
Simple metal electrode shows a potential drop in an electrolyte and the range of changes depends on the electrolyte composition, type of metal and the state of its surface. However, the potential drop is usually unstable and difficult to observe. The problem can be overcome by differential measurements using an ISFET and a Reference FET (REFET) devices. The REFET cannot be sensitive for the investigated ion (H^+ ion for instance) but should respond as the ISFET to the changes of voltage, current, temperature etc.. The differential signal gained from an ideal pair of ISFET and REFET is expected to be independent on fluctuation of the reference electrode potential [1].

The REFET devices obtained by means of deposition of an ion blocking layer on the active surface of the ISFET were criticized by Bergveld et al. for their instability [2]. The same working conditions for the REFET can be obtained only for an ion non-blocking layer. The authors have proposed deposition of a polymer layer (acrylate/polyHEMA) on the gate surface of the ISFET in order to convert it into the REFET.

There are many research groups which do work in the field of the REFETs technology. Chudy et al. developed a polyHEMA (poly(2-hydroxyethyl methacrylate)) membrane covered with lipophilic potassium salt (KTPCIPB) [3]. Lai et al. also used an ion-unblocking membrane [4]. They performed silylation of ISFET Si_3N_4 dielectric layer using HMDS in toluene and deposited PVC cocktails using different plasticizers.

Stoichiometric silicon nitride is widely used as H^+ ion sensitive layer. Infrared investigations have pointed out that nitride surfaces etched in diluted HF do not rapidly oxidise when subsequently exposed to either liquid H_2O or humid room air [5]. However, it has been found that an ultra-thin oxide-like layer forms when the etched surface is rinsed in

deionized H_2O . It indicates that SiH_x groups on the nitride surface are converted to $SiOH$ due to hydroxylation, which undergoes rapid hydrolysis.



Silicon dioxide as an ion-sensitive layer shows instability in comparison to silicon oxynitride. A relatively low sensitivity of 25mV/pH has been found for ISFET sensors manufactured in CMOS process, where the oxynitride layer was used [6]. The effect of silicon nitride surface oxidation has been discussed in this paper.

Experimental

ISFET devices developed and manufactured using the CMOS technology [7] have been used in the experiments. These n-type FETs have been fabricated using p-type $\langle 100 \rangle$ silicon wafers. A cross-section of the ISFET is shown in Fig. 1. The thermal dioxide layer (65 nm) covered with the LPCVD silicon nitride layer (65 nm) is used as a gate dielectric layer. N^+ doped diffusion paths connect source and drain regions to their back side Cr/Au contacts. A slightly n-doped ISFET channel conducts electric current even without gate polarization.

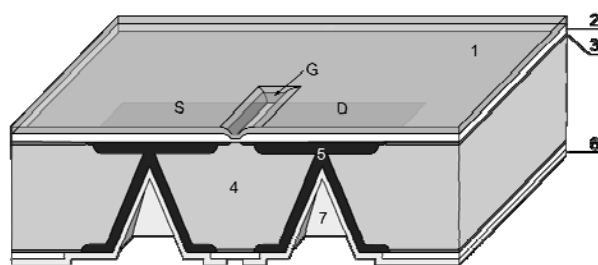


Fig.1. A cross-section of Back-Side Contact ISFET
Legend: 1-nitride layer, 2-silicon dioxide layer, 3- p^+ channel stopper, 4-p type substrate, 5- n^+ diffusion path, 6-Cr/Au metallization, 7-pyramid cavity.

The ISFETs have been basic devices for further fabrication of low sensitive (REFET) ones. Based on our previous studies on the nanowire sensors [8], a low temperature oxidation of the gate Si_3N_4 layer has been performed. The oxidation process has been carried out in a barrel-type plasma reactor PRS801 (Fig. 2a). The RF power of 450 W has been applied for 120 minutes. The plasma process made this way has purely chemical and isotropic nature. Reactive gas is driven into the barrel which acts as a Faraday cage. Thus, RF waves do not enter the treatment

chamber. Plasma UV radiation is not filtered and thermally activates the oxidation process. Finally the complete devices have been placed in modular flow packages, made of ABS resin (Fig. 3).

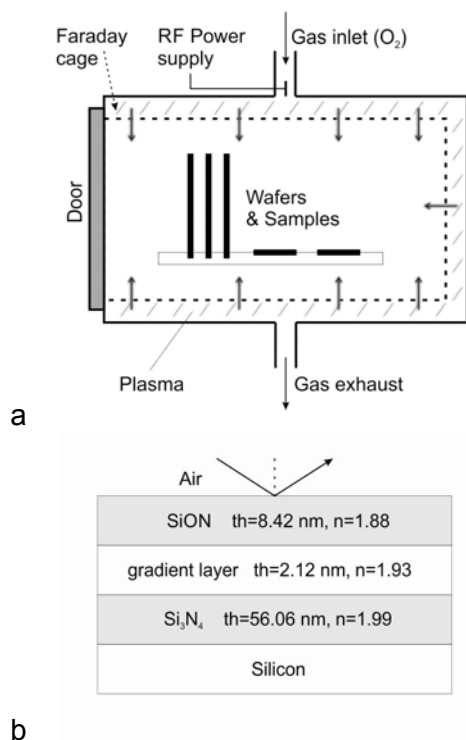


Fig. 2 a) Schematic view of the oxidation process in the plasma reactor; b) Optical model consisting of three layers. The best fitted thickness and refractive index parameters are inserted.



Fig. 3. Modular flow packages for ISFET and REFET sensors.

Results

Ellipsometric measurements

The effect of the oxygen plasma treatment on the surface of silicon nitride has been estimated using Sentech SE800 spectroscopic ellipsometer and silicon nitride covered test wafers. Plasma affected surface has been modelled as a layer formed by the stack of SiON and a gradient layer between SiON and Si₃N₄ (Fig. 2b). The optical properties of SiON and Si₃N₄ were described by a Tauc Lorentz model while the law of mixture used to model the equivalent dielectric function of the materials was the effective medium approximation of Bruggeman. The best fit (MSE=0.98) has been obtained for SiON, gradient layer and Si₃N₄ thickness of 8.42 nm, 2.12 nm, 56.06 nm respectively. The corresponding values of refractive index have been 1.88, 1.93 and 1.99.

Device performance measurements

All fabricated devices have been examined in a source follower circuit using $I_{ds}=100\mu A$ current. A general scheme of the circuit is presented in Fig. 4. For the first classification, the examined device has been connected in "ISFET" position, whereas the "REFET" device has been replaced with an adjusted resistor. It has made possible to tune of an operation point of the tested device into $-0.6V \dots +0.6V$ range. An Ag/AgCl reference electrode with a double KCl electrolyte has been used for polarization of the transistor liquid gate. Measurements have been conducted in a fluidic system assembled using the above presented flow cells (Fig. 5). Commercially available buffer solutions have been used for measurements of output signal versus pH. The fluidic system has been filled with a successive electrolyte and there has not been any flow during the measurements.

Typical ISFET sensor $I_{ds}(V_{ds})$ characteristics depend on concentration of H⁺ ions in a water solution that surrounds the gate dielectric. The source follower produces output voltage, which is an accurate copy of a transistor gate potential. Dependence of the output signal on pH of the solution has been measured every 30 seconds in 4-min. sessions after changing the buffer solution in the fluidic system. The signal corresponding to pH=7 has been adjusted near to 0mV by means of the resistor mentioned earlier. The measured values represented by the circular dots are shown in Fig. 6. The ISFET has revealed almost linear characteristics with sensitivity of 47mV per pH unit. Similar measurements obtained for the plasma oxidized device have given far suppressed pH dependence (square dots in Fig. 6). Three times lower pH sensitivity has been found for this kind of REFET-like device.

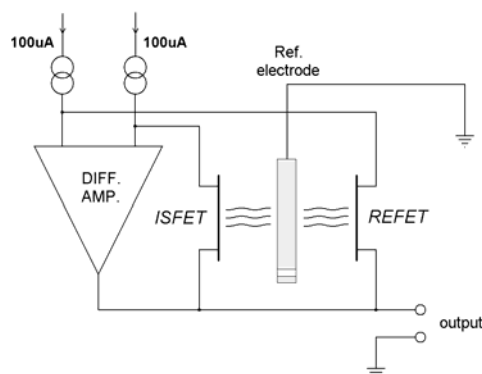


Fig. 4 Schematic diagram of source follower circuit for differential measurement.

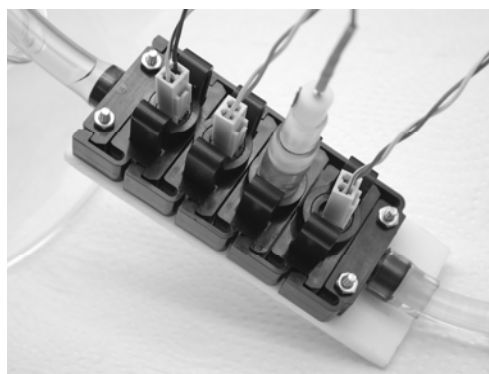


Fig. 5. View of the fluidic system.

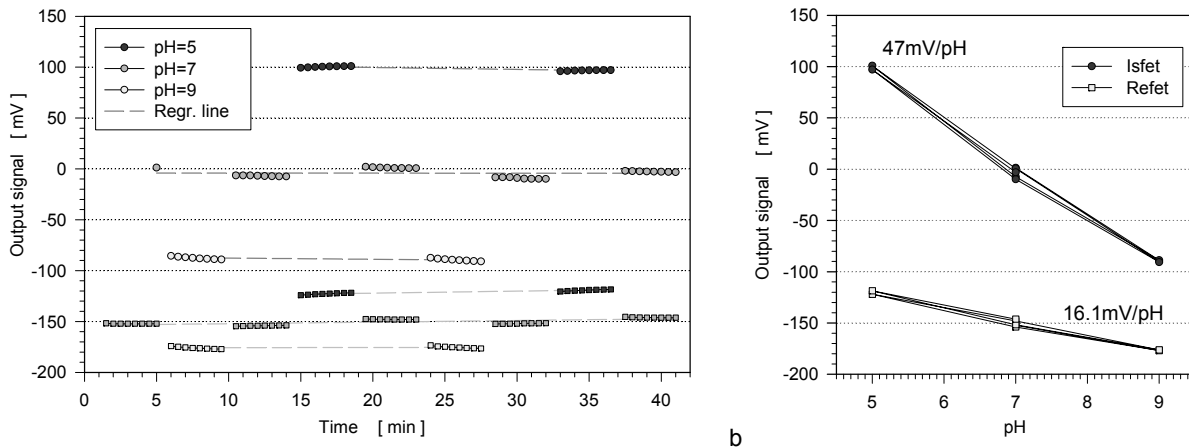


Fig.6 a) A comparison of pH responses for ISFET device (circular dots) and oxidized device (square dots) examined in 4 min. sessions in buffer solutions; b) Mean output signal calculated for three last points of the each session versus pH for the both devices.

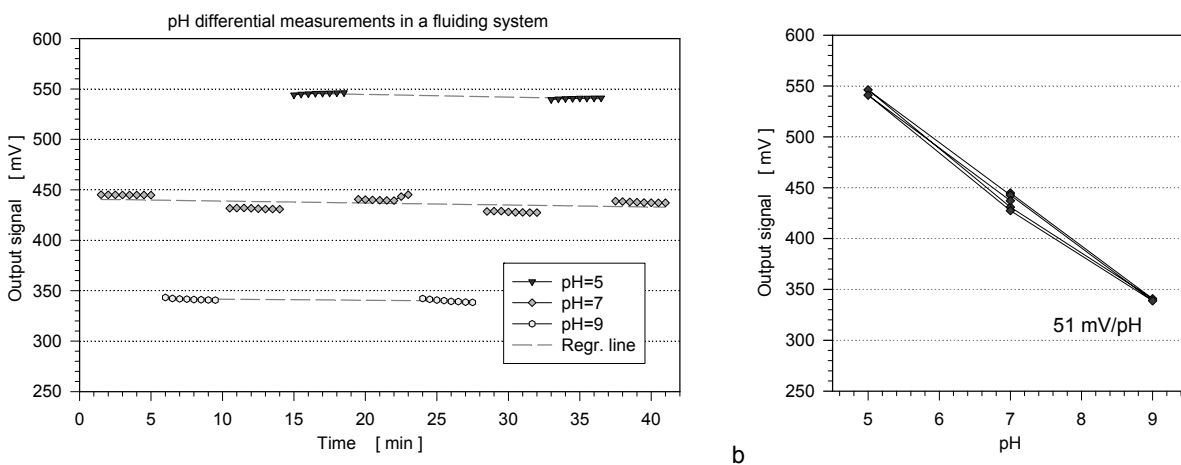


Fig.7 a) Differential measurements of pH of buffer solutions using a pair of devices that have been individually presented in Fig. 6; b) Mean output signal versus pH for these measurements.

Investigations of differential measurements of pH have been started using the circuit presented in Fig. 4. The individually characterized devices have been placed in flow cells on the left and right sides of the Ag/AgCl reference electrode cell (Fig. 5). Results of the measurement are presented in Fig. 7. A pair of the devices has indicated a stable response to the hydrogen ion concentration and the pH sensitivity has increased to 51mV per pH unit. The stability of the sensitivity factor has also been examined. Similar measurements have given sensitivity of 54.5mV/pH and 49.9mV/pH after two days and two weeks of storage in DI water, respectively. The simple differential measurement circuits has not allowed for offsetting the output signal. In order to produce a relatively small voltage, an initial selection of the ISFET/REFET pairs has been undertaken. The subsequent pair of the devices has revealed a pH dependence that is presented in Fig. 8.

It has been already mentioned that the differential pH measurement requires the reference electrode of lower stability than direct ISFET measurement. The stability of the gold and platinum thin film electrodes in water solutions was previously described by the authors [9]. A magnetron sputtered Pt electrode of the same sizes as ISFET chip has been examined in this work. The results obtained for the pH 5 buffer solution within ten minutes measurement of the potential difference between Ag/AgCl reference electrode and Pt quasi-reference electrode is shown in Fig. 9. An initial drop of 12mV during the first minute is followed by the

subsequent slight decrease of the potential difference, which is randomly influenced by fluctuations.

A usefulness of the Pt thin film electrode instead of Ag/AgCl electrode for pH estimation of buffer solutions has been verified (Fig. 10). Described above (pair of ISFET/REFET sensors and the differential measurement setup Fig. 8) have been used. The results do not fit pH changes of the solution but rather depends in a reproducible way on a material that is diluted.

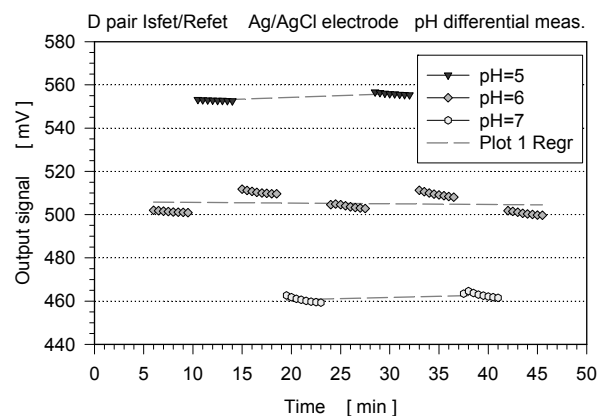


Fig.8. Differential measurements of pH of buffer solutions for a new pair of the devices .

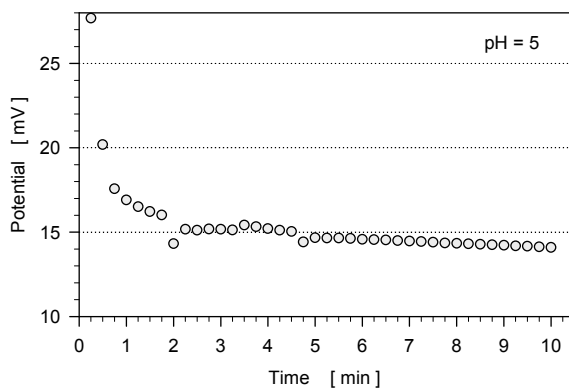


Fig.9. Pt-electrode potential versus time in pH=5 buffer solution.

Possibility of application of the Pt electrode in the differential measurement has been examined using hydrochloric acid solutions. Five solutions of the concentration ranging from 0.1M to 2.4M have been prepared. The measurements have been carried out using the setup and sensors mentioned earlier. The results and pH values calculated for a few specific molar concentrations are presented in Fig. 11. The experiment has confirmed close to linear dependence of the differential output signal for HCl concentrations equal or below 1 mole per dm^3 .

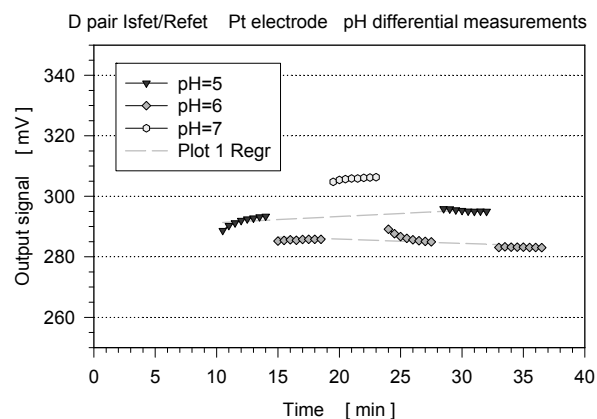


Fig.10 Results of testing of the differential measurement setup and Pt electrode in pH buffers.

The sensitivity of 55mV per pH unit has been achieved. Higher concentration, which gives a negative pH value, produces a signal that behaves unstable after two minutes of testing. Both the ISFET and quasi-REFET have worked repeatably during the experiments.

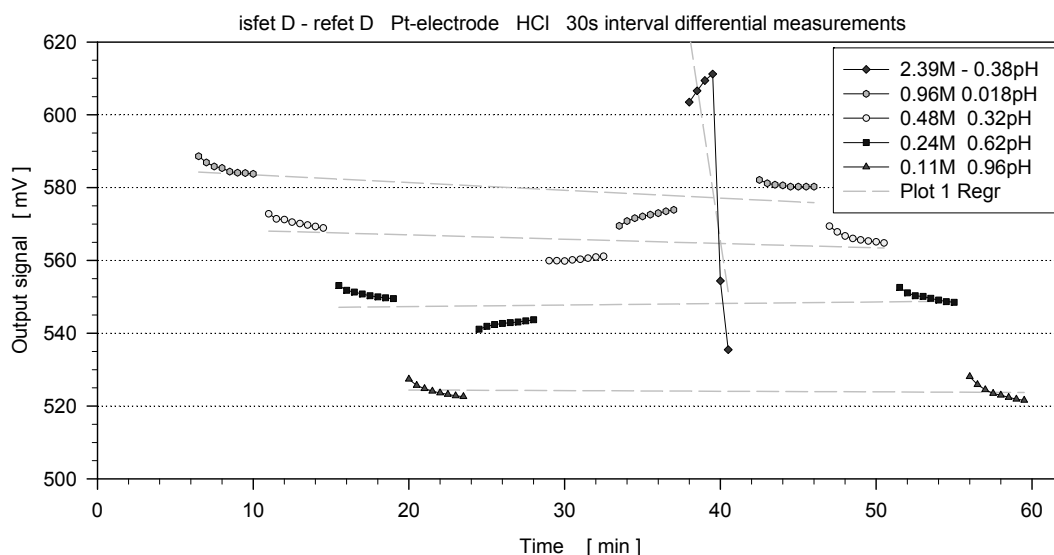


Fig.11. Output signal versus time of the differential measurements of diluted HCl samples. The same sensors and Pt-electrode have been used as in the previous experiment.

Conclusions

Fabricated using RF oxygen plasma REFET devices characterize by a little non-zero pH sensitivity, so they can be classified as quasi-REFETs. Nevertheless they have been positively verified in the differential measurements of pH value using a silver chloride reference electrode. Sensitivity in the range of $49 \pm 55\text{mV/pH}$ toward the H^+ ion concentration has been found. This value has been found to be several millivolts higher than sensitivity of the single ISFET. The quasi-REFETs can be applied in the differential measurements together with pseudo-reference Pt electrode instead of Ag/AgCl reference electrode. The application for investigation of HCl water solutions has given 55mV/pH sensitivity. However, pH changes must only be due to the ion concentration changes. The system cannot be applied if there is a change in chemical composition of the solution.

The REFETs cannot be rinsed with chemicals, which etch silicon oxynitride layer, for example HF acid.

The developed REFET devices can be easy manufactured in a standard CMOS-compatible technology or using the modified processing comprises the low temperature oxidation of the nitride dielectric ISFET. They can be used in any fluidic system in the same packages as ISFET devices. The two-week stability of the ISFET/REFET pair output signal has been positively verified.

The authors acknowledge mgr inż. Bohdan Jaroszewicz for ISFET selection and discussion.

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