pH Sensing Properties of ISFETs with LPCVD Silicon Nitride Sensitive-Gate

Paik-Kyun Shin, Thomas Mikolajick, and Heiner Ryssel

Abstract

Ion-Sensitive Field-Effect Transistors(ISFETs) with LPCVD silicon nitride as a sensitive gate were fabricated on the basis of a CMOS process. The silicon nitride was deposited directly on a poly silicon gate-electrode. Using a specially designed measuring cell, the hydrogen ion sensing properties of the ISFET in liquid could be investigated without any bonding or encapsulation. At first, the sensitivity was estimated by simulations according to the site-binding theory and the experimental results were analysed and compared with simulated results. The measured data were in good agreement with the simulated results. The silicon nitride based ISFET had good linearity evaluated from correlation factor(≥ 0.9998) and a mean pH-sensitivity of 56.8 mV/pH. The maximum hysteresis width between forward(pH = 3 → pH = 11)- and backward(pH = 11 → pH = 3) titration was 16.7 mV at pH = 6.54.

I. Introduction

In order to monitor the ion concentration of human-body fluids or electrolyte solutions there are recently numerous investigations based on various structures and materials.

The ISFET(Ion-Sensitive Field-Effect Transistor) is a solid-state chemical sensor which combines the chemical sensitivity of a membrane and the impedance transducing property of a MOSFET (Metal Oxide Semiconuctor Field-Effect Transistor)[1]. Its main advantages are rapid response, small dimension and low output impedance[2].

Moreover, thanks to their fabrication compatibility with IC-process technology, it is possible to integrate several sensors on one chip.

ISFETs are essentially a variant of MOSFETs in which the metal gate is substituted by a combination of ion-sensitive layer, electrolyte, and reference electrode. While the function of a MOSFET is governed by the properties of the MOS capacitor, the fuction of an ISFET is related to the EIS(Electrolyte Insulator Semiconductor) structure whose flat-band voltage is proportional to the surface potential of the sensitive layer, which is given by the ion activity in the electrolyte.

For the purpose of selecting the sensitive layer, the experiences from ISEs(Ion-Selective Electrodes) are adopted. The sensing mechanism of an ISFET differs however from that of an ISE. Moreover, insulating layers, which cannot be used for ISEs, can also be adopted for ISFETs. In the case of pH-ISFETs, Si_3N_4[3-5], Al_2O_3 [6], Ta_2O_5[7, 8], which are compatible with IC-technology, were the most successful sensitive layers for hydrogen ions, so far.

The pH-sensitivity of inorganic membranes is best decribed by the site-binding theory[9].

In this study, the silicon nitride layer used as sensitive membrane for pH-ISFETs was deposited by a LPCVD(Low Pressure Chemical Vapor Deposition) process. For the fabrication of the sensor device, a conventional CMOS structure was adopted and the fabrication process had minimum deviations from a standard CMOS process.

The pH-dependence of the surface potential variance of silicon nitride contacting electrolyte was simulated with our program EVIS(EValuation software for Ion Sensitive structures) on the basis of the site-binding theory.

In order to analyze the pH-sensing properties of ISFETs with silicon nitride sensitive gate, the drift/rate, pH-sensitivity and hysteresis of the sensor chip, and their long-term behaviour were investigated. All the measurements were carried out using a flow-through system. The background electrolyte was 0.5 M KCl with a buffer of 0.01 M Na_2HPO_4 / KH_2PO_4, and the desired pH value was achieved by adding 1 M HCl and 1 M KOH. The measured data were then analyzed and compared with simulated results.

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III. Device Design and Fabrication

1. Mask Design and Measuring Cell

It was aimed at assembling the bare ISFET structure in the measuring cell without any bonding and encapsulation.

The sensitive area of the sensor was placed in the middle of the chip, and the distance between the sensitive area and the contact pads was established sufficiently large in order to avoid a short between the measured liquid and the electronic contact in case of inexact alignment.

Moreover, long source and drain regions of the sensor transistor were used to achieve a flat surface in the area of the liquid seal. In order to accomplish an easy and safe electrical contact in the measuring cell, the contact pads were designed largely at the edge of the chip. There are two identical ISFET structures on one chip so that one of the two may be used in the future as a REFET (REference FET). Each ISFET was fabricated in a separate p-well.

The layout of the ISFET is shown in Fig. 1.

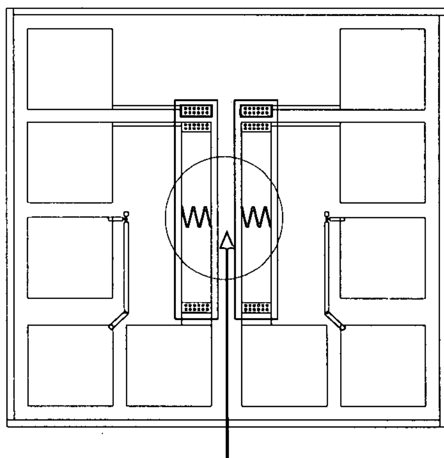


Fig. 1. Layout of the ISFET-sensor chip.

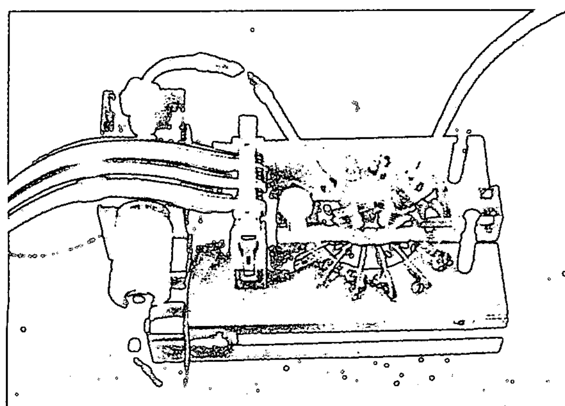


Fig. 2. The measuring cell.

Fig. 2 represents the measuring cell which is adopted in our study. The measuring cell is constructed from plexiglass and a compact reference electrode EP 23(Biometra, Germany) was mounted in it. The electrical contact of the chip was realized by blades which are generally used for electrical contacts in wafer probers.

The following goals are achieved by the meauring cell: an easy change of the chip, a housing for the reference electrode, a bubble free contact of measuring liquid with the gate of the ISFET and the reference electrode, an easy contact of aluminum chip pads, a minute dead volume in the channels, and a backside contact of the chip.

2. Fabrication of the ISFET Chip

For the purpose of using the ISFET's merit of compatability with conventional IC process fully, we have tried to minimize the additional sensor-specific process steps compared to conventional CMOS fabrication processes.

In the FET part of the ISFET chip, the very same processing steps of our MOSFETs were adopted. The major features of our process are a LOCOS isolation, a p-well, and a self-aligned poly silicon technology.

As a sensitive layer, a 65 nm thick layer of silicon nitride was deposited in a LPCVD process directly over the poly silicon gate-electrode. This direct deposition of the sensitive layer on the poly silicon electrode distinguishes our process from ISFET fabrication processes by other groups in which the poly silicon was etched[10] or a conventional Al-gate process was used[11]. Our method is more compatible with conventional CMOS processes and it realizes the simple integration of ISFETs in an existing CMOS process. A cross-sectional view of our ISFETs is shown in Fig. 3.

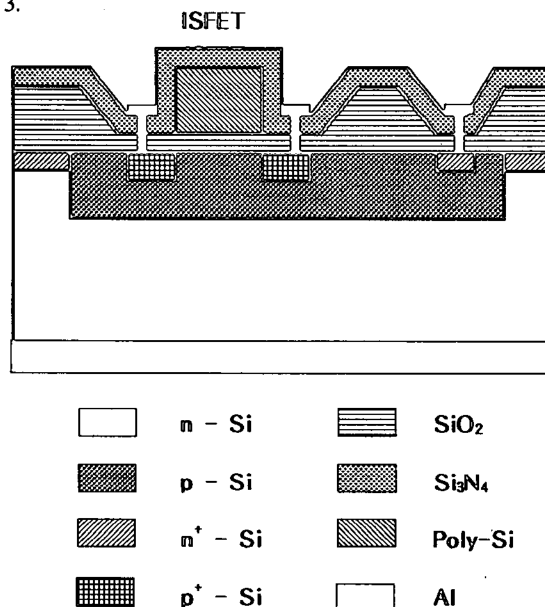
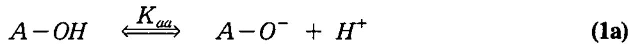


Fig. 3. A cross-sectional view of an ISFET.

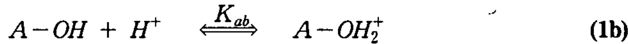
III. Simulation According to the Site-Binding Model

If an electrolyte is in contact with an insulator, no charge exchange between the insulator and the electrolyte occures. The electrochemical potential of the electrolyte and the insulator can, therefore, not be in equilibrium. This fact had disturbed the understanding of potential building of general dielectric materials which were introduced as sensitive layers for ISFETs. Siu[12] had succeeded in explaining the potential building at the electrolyte-insulator boundary by adopting the site- binding theory which had been developed previously by Yates et. al[13] in colloid chemistry.

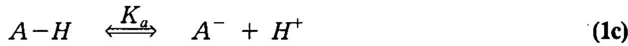
In Fig. 4, a schematic diagram of the site-binding model for a surface containing one amphoteric site can be seen. There can be three different types of sites on the insulator surface: acidic(AH), basic(BH^+), and amphoteric sites (AOH). Reaction equations for the equilibrium between the relevant surface groups and the H^+ ions located directly near the surface are given by equation (1a)-(1d), where K_{aa} and K_{ab} are acidic and basic reaction constants of an amphoteric site, and K_a, K_b are the reaction constants of acidic and basic sites, respectively.



$$A-OH \overset{K_{aa}}{\Longleftrightarrow} A-O^- + H^+ \quad (1a)$$



$$A-OH + H^+ \overset{K_{ab}}{\Longleftrightarrow} A-OH_2^+ \quad (1b)$$



$$A-H \overset{K_a}{\Longleftrightarrow} A^- + H^+ \quad (1c)$$

$$B + H^+ \overset{K_b}{\Longleftrightarrow} B-H^+ \quad (1d)$$

An exchange of hydrogen ions between the electrolyte and surface sites of the insulator results in a variation of the net surface charge q_o of the insulator. The sum of surface charge and the charge in the electrolytic double layer must be zero. Using Gouy-Chapmann-Stern theory, the surface potential of the insulator can be connected to the net surface charge of the insulator.

$$\Psi = \frac{qN_s q_o}{C_{st}} + 2\frac{kT}{q} \cdot \sinh^{-1}\left[\frac{qN_s q_o}{\sqrt{8kTc\varepsilon_w \varepsilon_o}}\right] \quad (2)$$

N_s : surface charge density of surface sites
C_{St} : Stern capacitance
c : ion concentration in the background electrolyte
ε_w : permittivity of water
ε_o : permittivity in vacuum

The relation between the pH of the electrolyte and the surface potential of the insulator Ψ is given by Eq. (3)[14].

$$2.303(pH_{zc} - pH) = \frac{q\Psi}{kT} + \ln[f(q_o)] \quad (3)$$

pH_{pzc} : pH at the zero point where net surface charge is zero

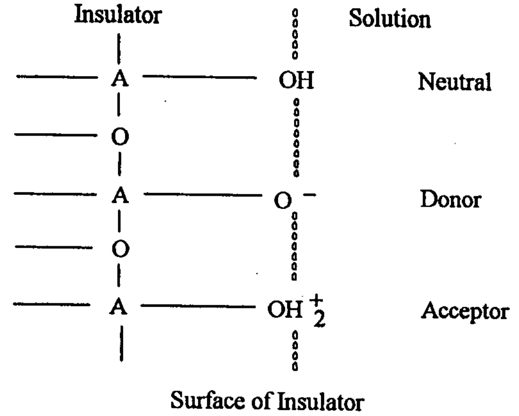


Fig. 4. A schematic diagram of the site-binding model.

q_o : net surface charge of the isolator
k : boltzmann constant
T : absolute temperature

The function $f(q_o)$ in Eq. (3) is given by one of the three Eqs.(4a, b, c) according to the type of site considered.

$$f(q_o) = \frac{\frac{q_o}{\sqrt{K_A}} + \sqrt{4(1-q_o^2) - \frac{q_o^2}{K_A}}}{4(1-q_o)} \quad : amphoteric\ sites \quad (4a)$$

$$f(q_o) = -\frac{1+q_o}{q_o} \quad : acidic\ site \quad (4b)$$

$$f(q_o) = \frac{q_o}{1-q_o} \quad : basic\ site \quad (4c)$$

$K_A = K_{aa}/K_{ab}$: reaction constant of amphoteric sites

On the basis of Eqs. (1) to (4), the pH dependence of the surface potential considering a single site can be evaluated.

In case of silicon nitride, there are two surface sites on the surface, namely the amphoteric silanol (SiOH) site and the alkalic amino ($SiNH_2$) site. Equation (3) must therefore be written for each surface site. In general, the relation between the function $f(q_o)$ of the (ν)-th - and the (ν+1)-th surface site is given by Eq. (5).

$$\frac{f_\nu(q_{o,\nu})}{f_{\nu+1}(q_{o,\nu+1})} = 10^{(pH_{pzc,\nu} - pH_{pzc,\nu+1})} \quad (5)$$

Harame et. al [15] have suggested an easy solution of Eq. (5). At first, the surface charge of a site can be used as a parameter and the value of $f_\nu(q_o,\nu)$ can be evaluated with Eq. (4). Equation (5) gives then the value of $f_{\nu+1}(q_o,\nu+1)$ and the charge of the (ν+1)-th site can be calculated by the inverse function $q_{o,\nu+1}(f_{\nu+1})$. This process can be repeated for all surface sites and then the whole surface charge can be evaluated by summing the charge of each surface site. We have written the simulation program EVIS (*EV*aluation software for *I*on sensitive *S*tructures) on the basis of the above mentioned procedure.

Fig. 5 represents the pH-response of the surface potential of a silicon nitride insulator theoretically. The theoretical pH-response of amphoteric sites and that of basic sites alone are also included. It can be seen that the linearity of the pH-response of an insulator, which has both surface sites, can be extended to the pH range of 0 to 14. The parameters which were used for the simulation are given in Table 1.

The sub-nernstian pH-sensitivity(≈ 55 mV / pH, at 25℃)[3-5] of silicon nitride can be explained by the combination of amphoteric silanol sites and alkalic amino sites.

The simulated pH-sensitivity of silicon nitride was 57.9 mV / pH at 25℃ and the combined pH_{ZC} was 5.8.

Ⅳ. Measurements and Analysis

As the hydrogen ion sensing operation of an ISFET should depend on the surface potential caused by the variation of ion concentration in the measured liquid, the ISFET device was always operated in constant charge mode, at which the drain current and the drain-source voltage were maintained constant, so that the electrical parameters of the FET could be disregarded. Fig. 6 represents the equivalent circuit diagram of an ISFET.

Using the reference electrode, a constant potential G was defined for the electrolyte. The potential V_M is the variable voltage component, which represents the essential property of the ISFET

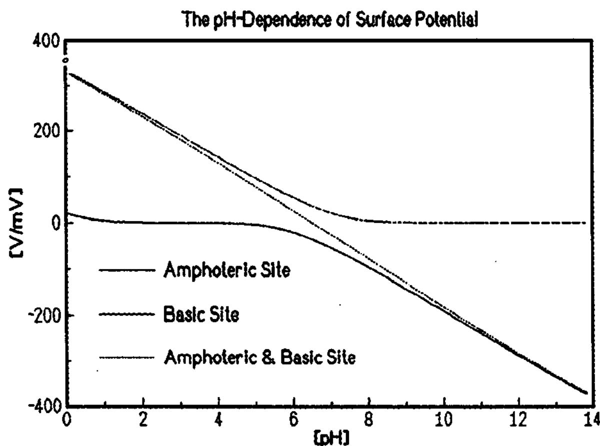


Fig. 5. The pH-sensitivity of the surface potential of an insulator with an amphoteric site, a basic site and an insulator with both sites on its surface.

Table 1. Site binding parameters for silicon nitride.

site	N_s / ㎠	pH_{zc}	pK_{al}	ΔpK_A
SiOH	$3 \cdot 10^{14}$ [15]	2.5 [12]		6.9 [6]
$SiNH_2$	$2 \cdot 10^{14}$ [15]		5.8 [16]	

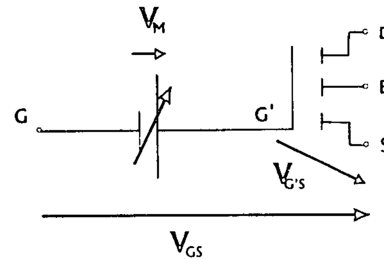


Fig. 6. The equivalent circuit diagram of an ISFET.

as an ion sensor, namely the potential variation on the surface of the gate insulator.

As the operation point of the ISFET device, I_D and V_{DS} were 95 μA and 100 mV, respectively. Since the naturally grown silicon dioxide on the surface of silicon nitride deteriorates the sensitivity and hysteresis property of the sensor, the surface of the silicon nitride gate was treated by HF(≤ 5%) for 1 min before the ISFET was assembled in the measuring cell. The surface potential variation through the pH variation of the electrolyte, the pH-sensitivity, the hysteresis phenomenon, and their long-term behavior were then analyzed.

The measured results are represented in Figs. 7, 8, and 9.

In order to investigate the hysteresis, the titration was carried out at first from pH = 3 to pH = 11(forward titration) and then repeated from pH = 11 to pH = 3(backward titration). The mean sensitivity at forward and backward titration were 57.0 and 56.6 mV / pH, respectively, which are almost the same as the simulated value, namely 57.9 mV / pH.

In Fig. 7 it is shown that the ISFET with silicon nitride sensitive layer has a good linearity of pH-sensitivity which was expected from simulations, and which is caused by the combinated function of an amphoteric and a basic surface site. The charge exchange between SiOH and $SiNH_2$ sites on the silicon nitride, which originates in different acidic and alkalic properties of both surface sites, results in a sub-Nernstian behavior of the pH-sensitivity of silicon nitride. The correlation factors for the evaluation of linearity are 0.9998 at both titrations. The mean deviation of surface potential from the mean sensitivity were 2.8 mV[pH3 → pH11] and 3.1 mV[pH11 → pH3] which corresponds to about 0.05 pH.

The hysteresis property of the ISFET-sensor can be seen more clearly in Fig. 8, where points at each pH value represent the deviation from the regression line. The hysteresis width in the region of neutral pH value is 17 mV and the mean hysteresis width is 10.2 mV.

The long-term behavior of an ISFET with a pre- etched pure silicon nitride layer can be seen in Fig. 9, where the variance of voltage at pH = 7, integral sensitivity at both titration, hysteresis at pH = 7 are re- presented for a period of 4 weeks.

The voltage at pH 7 showes a nearly linear drift. A one point calibration on a regular basis is therefore in need. The sensitivity

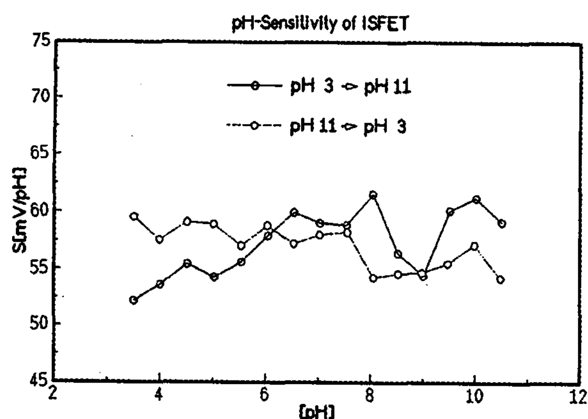


Fig. 7. The pH-sensitivity of an ISFET with Si_3N_4 sensitive gate.

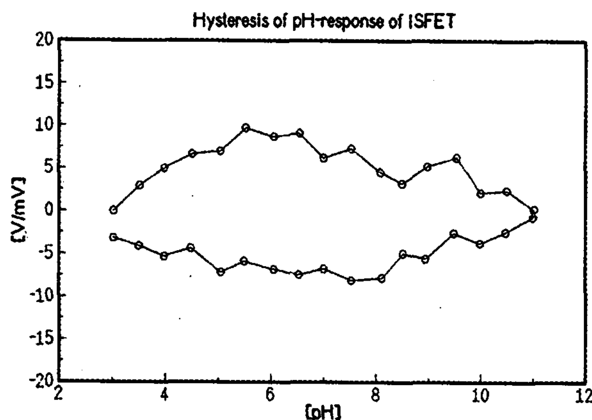


Fig. 8. The hysteresis of pH-sensitivity of ISFET with Si_3N_4 sensitive gate.

of silicon nitride varies only minutely with the lapse of time and the hysteresis width at pH 7, where our ISFET has the maximum hysteresis of pH-response, shows at most 6 mV deviation from the initial value. Therefore, our ISFET can be put into use for measurements over a period of at least 4 weeks, without repeating the treatment with diluted HF [$\leq 5\%$].

V. Conclusion

A ISFET with LPCVD silicon nitride sensitive layer was fabricated and the sensing properties for hydrogen ions in liquid were investigated.

Although the fabrication process of the sensor chip was more compatible with conventional CMOS process than that of other reported ISFETs[10, 11], the gerenal properties of our ISFET were similar to the properties found by other groups[3-5]. The mean sensitivity of 56.8 mV / pH and the good linearity of the surface potential variance according to the pH value of the liquid were nearly in accordance with the simulated results, which is based on the site-binding model. The mean hysteresis width of

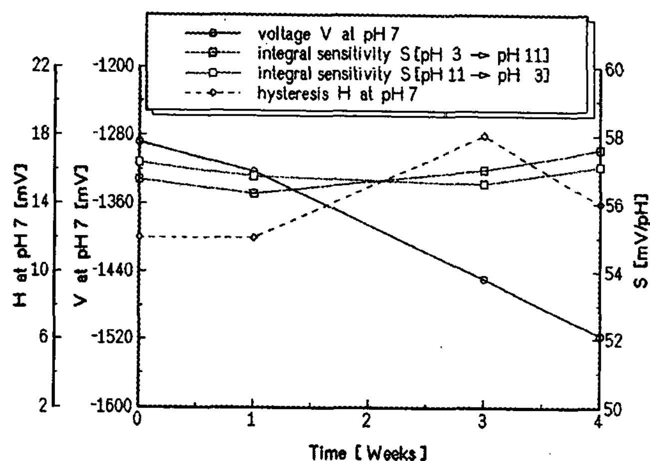


Fig. 9. The long-term behaviour of sensing properties of an ISFET with Si_3N_4 sensitive gate.

the ISFET in the pH-loop of pH 3 ↔ pH 11 was 10.2 mV. The ISFET could be used at least 4 weeks long without a repeated treatment with diluted HF.

The assembling of bare ISFET-chips in a flow-cell has the merits of a convenient measurement and the complicated encapsulation and bonding processes can be eliminated. Furthermore, a FIA (Flow Injection Analysis) system for the fast on-line monitoring and the good long-time stability can be designed on the basis of our dual-ISFET chip in which one of two ISFETs can be used as a ReFET(REference FET).

References

[1] P. Bergveld and A. Sibbald, *Analytical and biomedical application of Ion-Sensitive Field-Effect Transistors*, Elsevier, 1988, Volume XXII.

[2] T. Matsuo and M. Esashi, "Methods of ISFET fabrication", *Sensors & Actuators*, Vol. 1, pp. 77-96, 1981.

[3] F. Chauvet, A. Amari and A. Martinez, "Stability of silicon-nitride / silcondioxide / silicon electrodes used in pH micro-electronic sensors", *Sensors & Actuators*, Vol. 6, pp. 255-267, 1984.

[4] L. Bousse, J. Shott and J. D. Meindle, "A Process for the combined fabrication of ion sensors and CMOS circuits", *IEEE Electron Device Letters*, Vol. 9, No. 1, pp. 44-46, 1988.

[5] V. Rocher et. all., "Photho-CVD silicon nitride thin layers as pH-sensitive membrane", *Sensors & Actuators B*, Vol. 18-19, pp. 342-347, 1994.

[6] L. Bousse, N. F. de Rooij and P. Bergveld, "Operation of chemically sensitive Field-Effect Transistors as a function of the insulator-electrolyte interface", *IEEE Trans. Electron. Devices*, Vol. 30, No. 10, pp. 1263-1270, 1983.

[7] M. Teravanithorn, Y. Miyahara and T. Moritzmi, "The stability of Ta_2O_5 as a solid-state ion-sensitive membrane",

Japan J. Applyed. Phyics., Vol. 26, No. 12, pp. 2116-2120, 1987.

[8] A. S. Poghossian, "The super-Nernstian pH sensitivity of Ta_2O_5- Gate ISFETs", *Sensors & Actuators B*, Vol. 7, pp. 367-370, 1992.

[9] C. D. Fung, P. W. Cheung and W. H. Ko, "A generalized theory of an electrolyte-insulator-semiconductor Field-Effect Transistor", *IEEE Trans. Electron Devices*, Vol. 33; No. 1, pp. 8-18, 1986.

[10] H. S. Wong and M. H. White, "A self-contained CMOS Integrated pH Sensor", *IEDM Techn. Digest*, pp. 1807-1818, 1988.

[11] P. Berg, "Entwicklung einsatzfähiger Flüssigkeitssen-soren auf Feldeffekttransistorbasis mit Hilfe eines speziellen CMOS-Technologie-Prozesses", Ph. D. Theis, Faculty of Electrical Engineering & Informatical Engineering, *TU München*, 1989.

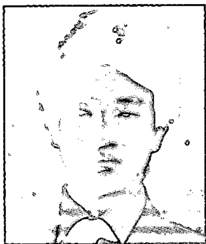
[12] W. M. Siu and R. S. C. Cobbold, "Basic properties of the electrolyte-SiO_2-Si system:physical and theoritical aspects", *IEEE Trans. Electron Devices*, Vol. 26, pp. 1805-1815, 1979.

[13] D. E. Yates, S. Levine and T. W. Healy, "Site-binding model of the electrical double layer at the oxide / water interface", *J. Chem. Soc., Faraday Trans. I*, Vol. 70, pp. 1807-1818, 1974.

[14] D. Harame, "Integrated circuit chemical sensors", Ph. D. Thesis, *Stanford Univ.*, 1984.

[15] D. L. Harame, L. J. Bousse, J. D. Shott and J. D. Meindl, "Ion sensing devices with silicon nitride and borosilicate glass Insulators", *IEEE Trans. on Electron Devices*, Vol. 34, No. 8, pp. 1700-1706, 1987.

[16] Y. Vlasov, A. Bratov, M. Sidorova and Y. Taranov, "Investigation of pH-sensitive ISFETs with oxide and nitride membranes using colloid chemistry methods", *Sensors & Actuaors B*, Vol. 1, pp. 350-353, 1990.



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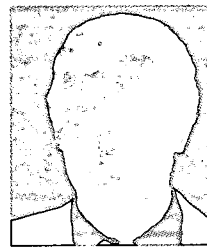

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