

Si-Based Electrodes for Potentiometric Measurements of Aqueous Solutions

Michał Zaborowski, Daniel Tomaszewski, Bohdan Jaroszewicz, and Piotr Grabiec

Abstract— Three sensors for chemical and physical examination of aqueous solutions were presented in the paper. An Au potentiometric electrode, an AgCl chlorine ion sensor and a p-n junction thermometer were developed. Their layout and internal structure were explained in the light of the manufacturing process. The device characteristics were measured in conditions corresponding to normal operation of the devices. Basic electrical parameters of the developed structures, as well as their sensitivity to environmental parameter variation were estimated.

Keywords— chlorine ion sensor, potentiometric sensor, p-n junction thermometer.

1. Introduction

Potentiometric sensors allow for easy measurements of ion concentration in aqueous solutions. They work in a range of sensitivity that is important in nature sciences [1]. The sensors have been developed on the basis of gold electrodes and covered with membranes sensitive to dedicated ions. Measurements are carried out in a circuit containing a reference electrode placed in the solution together with the sensor. The resulting electromotive force (EMF) is directly dependent on the ion concentration. Changes of ambient temperature usually influence the sensor output signal level and its sensitivity. In the presented work, an Au potentiometric electrode, a Cl^- ion sensor and a thermometer chip have been developed.

2. Device Fabrication

Gold electrodes were designed as basic devices suitable for potentiometric measurements. They were manufactured using n-type $\langle 100 \rangle$ oriented silicon wafers of low resistivity ranging from 0.01 to 0.001 Ωcm . A simple planar technology based on the complementary metal oxide semiconductor (CMOS) process was developed. First, a 100 nm thick thermal silicon dioxide layer was grown and a 65 nm thick silicon nitride layer was deposited using low-pressure chemical vapor deposition (LPCVD). Next, square 1×1 mm contact holes were photolithographically defined and opened. The Si_3N_4 layer was removed by plasma etching, whereas the SiO_2 layer was removed by wet etching. Afterwards, a Cr/Au double layer was sputtered to cover the top and bottom wafer surfaces. The thickness of

the chromium and gold layers was 10 nm and 500 nm, respectively. The electrodes were patterned at the top surface by means of photolithography followed by wet etching of Au and Cr layers. Post-metallization annealing at 340°C in nitrogen was performed in order to minimize the series resistance of the electrodes. A cross-section and simple topology of the gold electrode is shown in Fig. 1. Finally, the wafers were diced into separate square 4.9×4.9 mm chips.

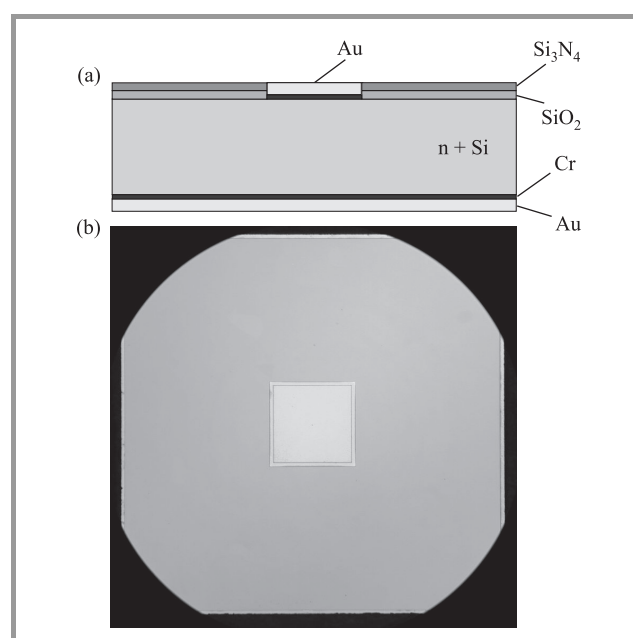


Fig. 1. A schematic cross-section (a) and top view of gold potentiometric electrode (b).

The gold electrodes were designed for operation in aqueous solutions. They could be covered with a variety of ion-sensitive membranes by sensor developers and users. Our efforts were concentrated on a small and stable value of series resistance of the device. An example of the on-wafer distribution of the measured Au electrode resistance has been shown in Fig. 2. The mean value of the resistance was about 30 m Ω . Also the deviation of the distribution from its mean value was reasonably small (about 5 m Ω).

Another type of the device for potentiometric measurements was the chlorine potentiometric sensor, designed based on the above-described gold electrodes. After the process of annealing in nitrogen ambient the silicon wafers

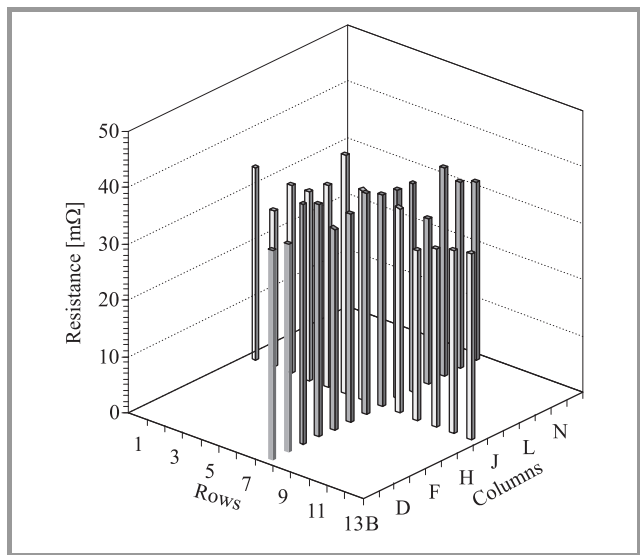


Fig. 2. On-wafer distribution of Au potentiometric electrode resistance.

with Au electrodes were subjected to a short etching step in a buffer HF solution. Next, two electrochemical processes were performed. First, backsides of the wafers were masked with a resist layer while the patterns at the front sides were Ag-electroplated. The process was optimized towards fine morphology of Ag grains (Fig. 3). Next, the 5 μm thick silver layer was partially electrochlorinated.

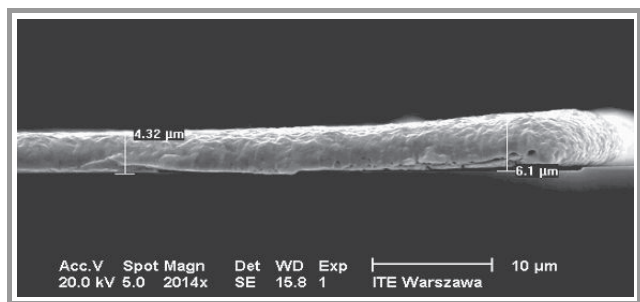


Fig. 3. Side view of the chlorine potentiometric sensor. Fine Ag layer morphology is visible.

Finally, the resist layer covering the backsides was removed in acetone bath, and the wafers were diced into chips. The topology of the top side of the device together with its cross-section has been presented in Fig. 4.

As mentioned above the potentiometric measurements required parallel observations of the temperature, which might influence measurements of ions. For this reason a p-n junction-based thermometer was designed and fabricated. It is known that thermal properties of the forward-biased p-n junction depend on the supplied current and on the doping distributions. Thus, in the first step a series of numerical calculations using the ATHENA/SSUPREM4 were done. Their purpose was to optimize the sensitivity (which in theory is of the order of $-(2-3)$ mV/deg) and linearity. The results of these calculations are shown in Fig. 5.

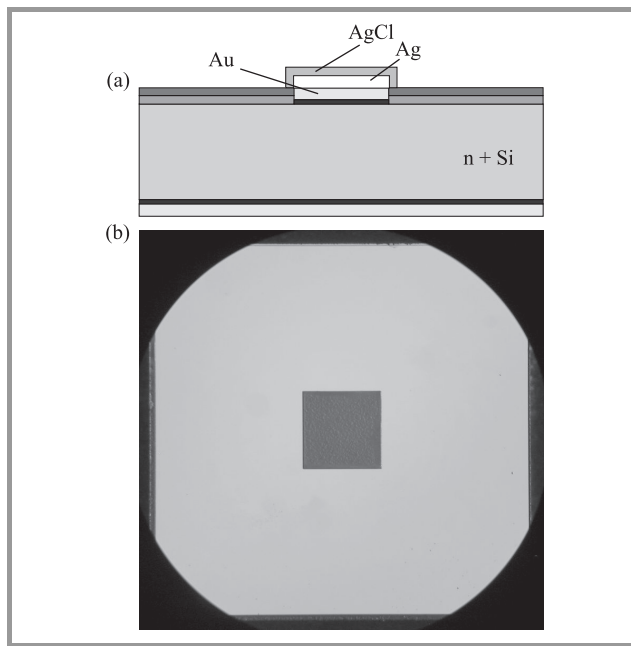


Fig. 4. A cross-section (a) and top view of the chlorine potentiometric sensor (b).

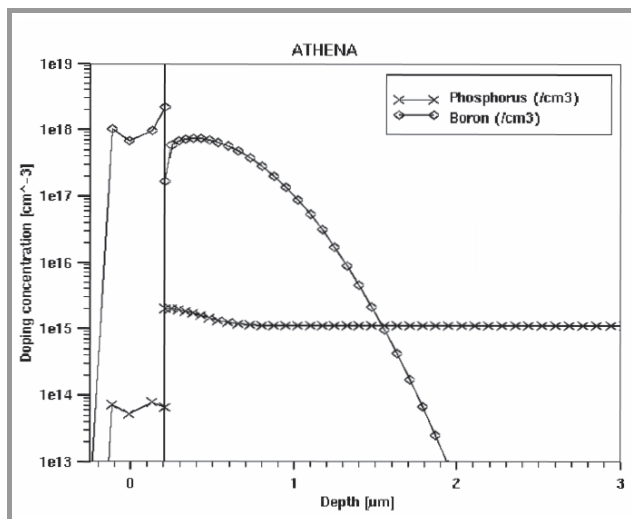


Fig. 5. Doping distribution in the p-n junction based thermometer calculated numerically using the ATHENA/SSUPREM4 solver.

The thermometer design was based on the following requirements: low electrical resistance between the sensor and the contact areas, and low thermal resistance between the sensor and a tested fluid. Therefore, the thermometer structures were fabricated in silicon membranes (Fig. 6). The chips were manufactured using $3-5 \Omega\text{cm} < 100 >$ oriented n-type silicon wafers. In the first step the silicon was thinned to a 100 μm membrane at the centre of the device by means of an anisotropic etch. A Si₃N₄ layer served as the mask against the etching. Next, the anode region was defined at the bottom side of the device. A $8 \cdot 10^{13} \text{ cm}^{-2}$ dose of boron ions was implanted into the anode area with 130 keV energy. Diffusion at 1000°C was used subsequently to form the p-n junction.

Next, phosphorus implantation (80 keV , $5 \cdot 10^{15} \text{ cm}^{-2}$) was employed to create the subcontact layer to the cathode of the sensor.

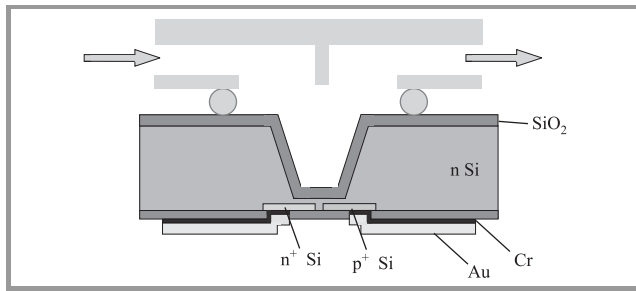


Fig. 6. Cross-sections of the p-n junction based thermometer working in a dedicated flow package.

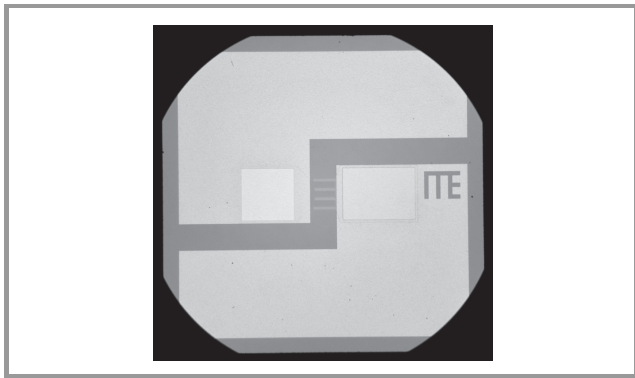


Fig. 7. View of the thermometer based on p-n junction.

Finally, Al contacts of the sensors were formed and the wafers were diced into chips. The thermometer chip layout is shown in Fig. 7.

3. Electric Measurements

The devices described in the previous section had a common topology (size, placement of contacts). Therefore, they were very well suited for operation in identical packages. Such a package was designed for measurements of ions under fluid flow conditions. Five sensor cells together with the reference electrode cell are presented in Fig. 8.

The AgCl potentiometric electrodes were destined for operation as Cl^- ion sensors in aqueous solutions. Four water solutions of KCl with different Cl^- ion concentrations were used in the experiments. The sensors worked in the flow packages, which were joined in series together with the reference electrode (as shown in Fig. 8). Obviously the sensors were uniformly distributed along the fluid flow. The output signals, i.e., the electromotive force (EMF) between the electrodes and the reference electrode were registered by a control application prepared in the LabView environment. The results are shown in Fig. 9.

The AgCl sensors exhibited log-lin reversible response to chlorine ion concentration. The sensitivity of the sensors in the higher range of Cl^- concentration was found to be

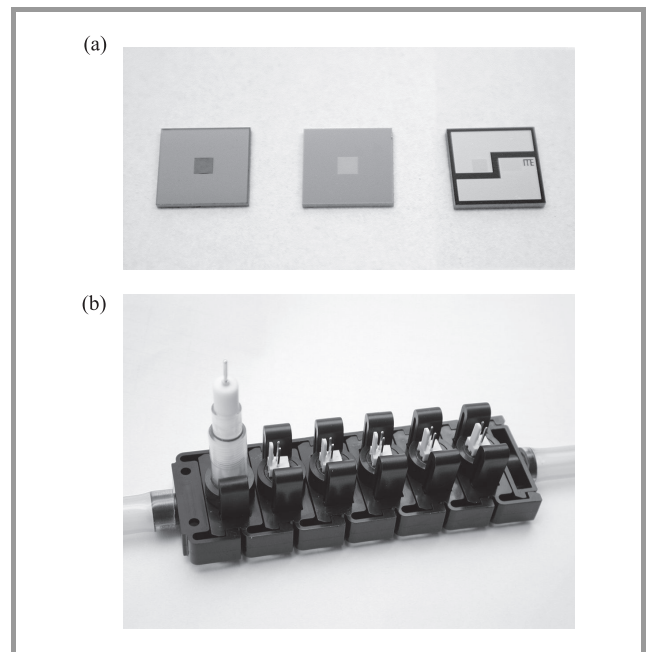


Fig. 8. Sensor devices (a) and a package for potentiometric measurements under fluid flow conditions (b).

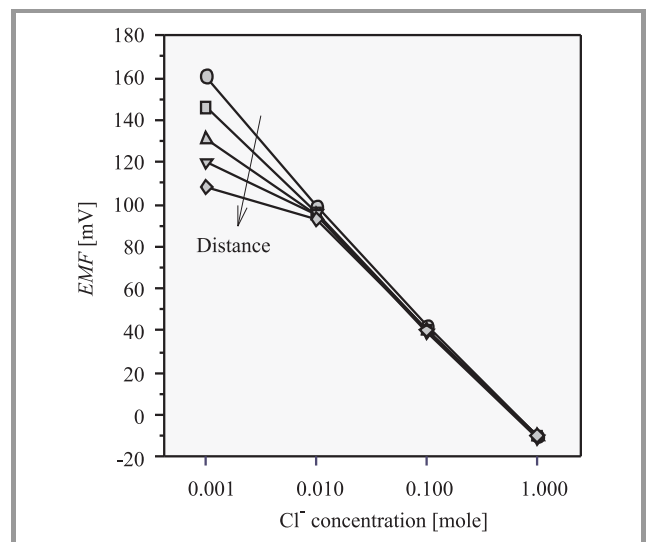


Fig. 9. Output signal versus Cl^- ion concentration for five AgCl electrodes assembled in the package for potentiometric measurements under fluid flow conditions.

close to the theoretical value of 57 mV/dec . However, in the case of sensors more distant from the reference electrode and for very diluted solutions a discrepancy from the log-lin behavior might be noticed. It may be explained by a simple model shown in Fig. 10. Here the variable meaning is as follows: V is an ideal voltmeter, R_V is its internal resistance, n denotes ion concentration, E is the measured electromotive force, R_{sol} denotes the resistance of the solution between the reference and the AgCl electrodes, X is the distance between them, and α , β , n_0 denote constants. According to this simple model the measured voltage starts to differ from the electromotive force if measured in a very

diluted solution or if the sensor is placed far away from the reference electrode. In both cases the solution resistance becomes non-negligible as compared to the internal resistance of the voltmeter. A giga-ohm class voltmeter is recommended for potentiometric measurements.

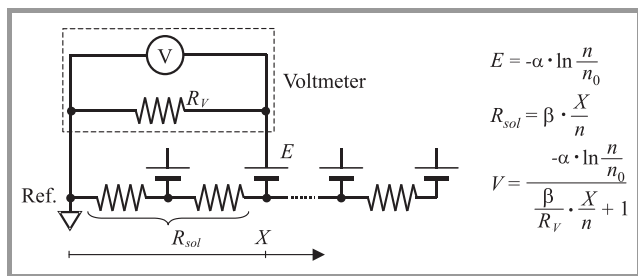


Fig. 10. A simple model of the Cl⁻ ion measurement setup using a number of cells.

The temperature sensors were the third set of devices to be subjected to electrical measurements. They were tested using different setups, i.e., before dicing on a hot plate, and after dicing and assembling in the package shown in Fig. 8. The temperature of the hot plate was controlled by a thermocouple within the chuck. Therefore, there was a small difference between the thermocouple and the wafer surface temperatures.

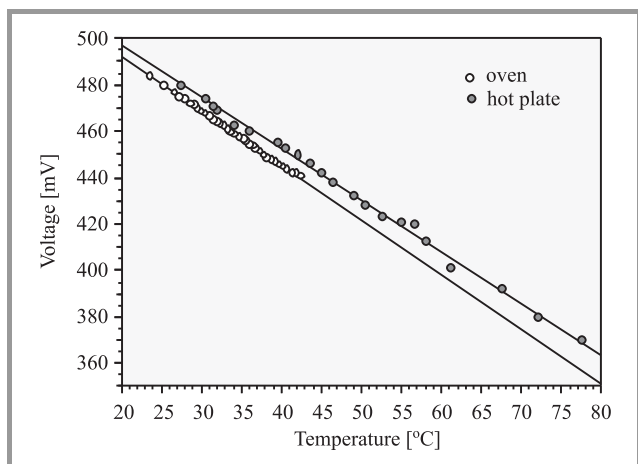


Fig. 11. Output signals versus temperature for the p-n junction-based thermometer measured on a hot plate (closed dots); in an oven (open dots).

Direct testing of the temperature sensors in the flow cell under water flow conditions was found to be difficult because of ambiguous recording of device temperature. Inlet and outlet temperatures differed by more than 3°C in experiments with 40°C water temperature. There was no possibility to install any temperature control equipment inside the package. As thermosensors might be used not only in the aqueous environment but in the air as well, they were calibrated in the packages placed in an air oven (Fig. 11). The obtained calibration characteristics $V(T)|_{I=100\mu A}$ revealed the satisfactory linearity with the -2.38 mV/deg slope, which was close to the theoretical value. Small heat

capacity and low heat resistance between the p-n junction and device surface should be emphasized.

4. Summary

In the presented work, the development of an Au potentiometric electrode, a Cl⁻ ion sensor and a thermometer chip is described. The technological process sequence, measurement procedures and results are reported. The electrical parameters and their spread have been examined in conditions corresponding to normal operation of the devices. The satisfactory on-wafer spread of series resistance of the gold electrodes, the measured sensitivity of AgCl electrodes to chlorine ion concentration, and the observed response of the thermometer structures have confirmed advantages of the developed technologies. Moreover, the standardization of the sensor chip layout and packaging make them a useful tool set suitable for environmental parameter observation.

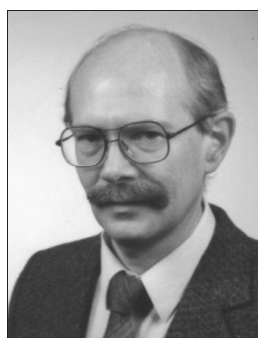
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Michał Zaborowski received the M.Sc. degree in solid-state electronics from the Warsaw University of Technology, Poland, in 1974. In 1976 he joined the Institute of Electron Technology (IET), Warsaw. He worked on IC metallization technology and received the Ph.D. degree in the IET, in 1998. His research interests include nanotechnology, micromachining and microsensor technology, particularly for biological applications. He is the author and co-author of more than 60 papers and conference presentations.

e-mail: mzab@ite.waw.pl
 Institute of Electron Technology
 Lotników av. 32/46
 02-668 Warsaw, Poland



Piotr B. Grabiec graduated from the Warsaw University of Technology, Poland, in 1973, and received the Ph.D. degree in chemistry from the same university in 1985. In 1974 he joined the Institute of Electron Technology, Warsaw, where he was involved in CVD and diffusion technology research. Since 1999 he has been the Head of

Silicon Microsystem and Nanostructure Department. His present activity involves fabrication of silicon ASICs, optoelectronic devices and MEMS and their integration. He has been involved in 10 EU projects and has been awarded numerous awards for development and commercialization of advanced micro-devices. He is the member of IEEE and Electrochemical Society. He is the author and co-author of more than 300 scientific papers and conference presentations. He holds 19 patents.

e-mail: grabiec@ite.waw.pl
 Institute of Electron Technology
 Lotników av. 32/46
 02-668 Warsaw, Poland



Bohdan Jaroszewicz received the M.Sc. degree in electronics from the Warsaw University of Technology, Poland, in 1968. He joined UNITRA-CEMI (Semiconductor Device Factory) in 1968 and was involved in a variety of research, engineering and fabrication activities related to MOS integrated circuits. As the engineering

section manager he was responsible for optimization of MOS IC yield. He joined the Institute of Electron Technology in Warsaw, in 1997. His main research interests are ion implantation engineering, as well as design, fabrication and characterization of ISFETs and ionising radiation detectors.

e-mail: bjarosz@ite.waw.pl
 Institute of Electron Technology
 Lotników av. 32/46
 02-668 Warsaw, Poland

Daniel Tomaszewski – for biography, see this issue, p. 49.