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A pH Sensitivity Control Method Using Hydrogen Annealing for Reference Field-Effect Transistors

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Many studies have been carried out on the use of ion-sensitive field-effect transistor (ISFET) and reference FET (REFET) devices for pH measurements. In previous works, different materials were used for the sensing membranes of ISFET and REFET devices so that the pH sensitivity of the REFET was much less than that of the ISFET. In these cases, it proved difficult to cancel out the variation in the AC voltage component in the solution by synchronizing the output signals of the REFET and ISFET. Therefore, we put forward a new proposal, in which we use hydrogen annealing to decrease the pH sensitivity of a Si_3N_4 film. Devices comprising Si_3N_4 on SiO_2 on n-type Si substrates were fabricated. The pH sensitivity of a device annealed in hydrogen for 20 min at 400 °C was reduced from 54.6 to 32.6 mV/pH. A higher temperature annealing was largely ineffective in producing greater decreases in sensitivity, and the annealing affected only the surface of the Si3N4 film, not its interior. We succeeded in developing the fabrication technology for a device with low pH sensitivity to be used as a REFET.

1. Introduction

The measurement of pH using ion-sensitive field-effect transistors (ISFETs)(1–3) is one of the most important techniques used to analyze biological and chemical reactions(4) in medicine, environmental science, and agriculture. In these fields, in situ measurements are required to carry out long-term monitoring. However, the external reference electrodes used, such as Ag/AgCl electrodes in KCl solution,(5,6) Ag/AgCl electrodes

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*Corresponding author: e-mail: futagawa@batonzone.tut.ac.jp without KCl,(7) and Pt electrodes,(8) are not without their problems; for example, the KCl solution for the Ag/AgCl electrode needs to be replenished, while the Ag/AgCl electrode without KCl cannot be used for long-term measurements. As an alternative, reference electrodes based on FETs, known as reference FETs (REFETs), have been studied. The required characteristic of the REFET is that it is less sensitive to pH than the ISFET. To achieve this, several types of REFET(9,10) device with different sensing membranes have been proposed: a polyacrylate (polyACE) type,(11) a polyvinyl chloride (PVC) type,(12,13) a parylene type,(14) and a SiO_2 type.(15) In all these cases, the sensing membranes of the ISFET and REFET were made of different materials, for example, an ISFET with a Si_3N_4 membrane and a REFET with a PVC membrane. This made it difficult to cancel out the variation in the AC voltage component in the solution, because of the different threshold voltages and transconductances of the REFET and ISFET.

Our group has been investigating pH sensors for in situ continuous measurements of the activity of cells in medicine,(16,17) the soil environment in agriculture,(18) and the physical condition of domestic animals.(19,20) However, external reference electrodes were used for the pH measurement, which restricted the measurement and experimental conditions for these in situ continuous measurements. Thus, we have been investigating a new approach in which a REFET with the same sensing membrane (Si_3N_4) and structure as the ISFET is used. The sensing membrane of the REFET is less sensitive to pH than that of the ISFET. However, the threshold voltages and transconductances of each device are the same, which makes it is easy to compensate for the variation in the AC voltage component. In this study, we proposed reducing the pH sensitivity of the REFET by hydrogen annealing. The Si_3N_4 film was annealed and capacitance-voltage profiling was used to measure the variation in threshold voltage with pH.

2. Concept of Reducing the pH Sensitivity by H_2 Annealing

Many materials, such as Si_3N_4, Al_2O_3, and Ta_2O_5, are used as the sensing membranes for ISFET pH sensors.(2,21) In this study, we focused on Si_3N_4 since this is compatible with Si complementary metal-oxide-semiconductor (CMOS) large-scale integrated (LSI) process technology.

According to the site-binding theory, silanol sites, Si-OH, and basic primary amine sites, Si-NH_2, are present on the surface of Si_3N_4 films.(22–24) Both sites are more sensitive to hydrogen ions (H^+) than to other ions,(24–26) such as Na^+ and K^+. Therefore, the Si_3N_4 film can be used to monitor the pH of a solution. In this case, the sites easily bond with and easily dissociate from hydrogen: therefore, the changes in pH can be measured using the film.

Hydrogen annealing is often used in Si CMOS-LSI fabrication processes to reduce the defects between the gate oxide and the Si substrate.(27,28) In this case, the defects are terminated by hydrogen atoms, which otherwise would be a source of increased variations in the threshold voltage of MOSFETs and give rise to leakage current in bipolar transistors.

We focused on this mechanism. If the Si-OH and Si-NH_2 sites on the Si_3N_4 surface were to be terminated by hydrogen atoms, would the pH sensitivity be decreased? If this mechanism can be realized with Si_3N_4, a REFET with the same structure as an ISFET could be fabricated simultaneously with the ISFET using a CMOS-LSI process, as shown in Fig. 1. This is the structure we propose for a future device, and is based on our

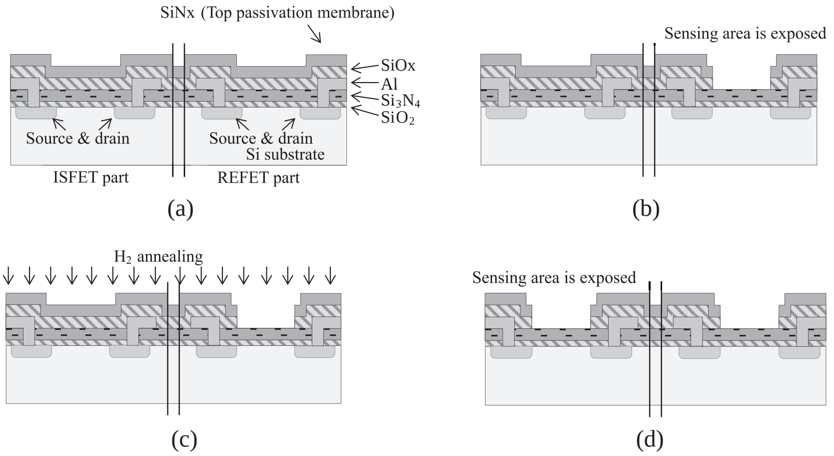


Fig. 1. Illustration of CMOS compatible LSI fabrication process for proposed integrated sensor comprising an ISFET and a REFET. (a) Conventional sensor structure after deposition of top SiN_x passivation layer. (b) Etching to surface of Si_3N_4 to expose REFET sensing area. (c) H_2 annealing to recover defect of interface between Si and SiO_2 and to terminate surface of REFET sensing membrane. (d) Etching to expose ISFET sensing area.

conventional structure. The only additional step, compared with the ISFET fabrication process, is the formation of an aperture over the REFET sensing area, as shown in Fig. 1(b). In this study, to confirm the feasibility of this type of device, we performed basic experiments in which we measured the pH sensitivities of simple membranes with and without hydrogen annealing.

3. Fabrication

The sensing area of the ISFET/REFET was replicated by a simple structure fabricated using CMOS-LSI technology. Figure 2 shows the fabrication process. N-type Si of 3.5 Ωcm was used as the substrate. First, a 52-nm-thick layer of SiO_2 was grown on the Si surface to anneal at 1000 °C with gas flows of O_2 at 250 L/h and H_2 at 250 L/h, as shown in Fig. 2(a). Next, a 150-nm-thick Si_3N_4 sensing membrane was deposited by thermal LPCVD at a pressure of 1.9 mPa, temperature of 850 °C, and gas flows of SiH_2Cl_2 at 200 sccm and NH_3 at 550 sccm, as shown in Fig. 2(b). In the next step, the samples were divided into two, such that some samples were annealed in hydrogen while other samples were unannealed, as shown in Fig. 2(c). The back sides of all the samples were abraded to break through the SiO_2 and Si_3N_4 on the backs of the chips, which were then attached to Au chip-mounted electrodes on a PCB substrate, as shown in Fig. 2(d). The contact between each chip and the electrode it was mounted on was ohmic. Finally, the sides of the chip and the chip mounting area were covered with an adhesive bond for waterproofing, as shown in Fig. 2(e). Figure 3 shows a photograph of a fabricated device. The lead wire is connected to the Si substrate through the chip-mounted electrode. For the pH sensitivity experiments, a KCl solution was dropped onto the surface of the chip, and a voltage was applied to the solution using a Ag/AgCl electrode. The experimental results are given in the next section.

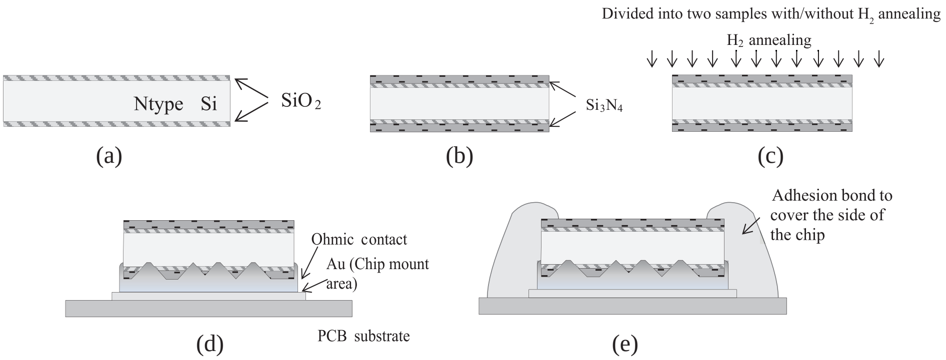
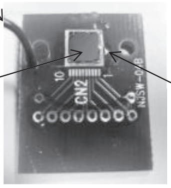


Fig. 2. Schematic diagrams showing fabrication process for experimental devices. (a) Thermal oxidation to grow 52-nm-thick SiO_2 layer. (b) Deposition of 150-nm-thick Si_3N_4 layer by thermal LPCVD. (c) H_2 annealing. (d) Chip mounted onto PCB substrate. (e) Adhesive bonding to cover sides and mounting area of chip.



Lead wire
(connecting to chip
mount electrode)

Chip (surface
was exposed)

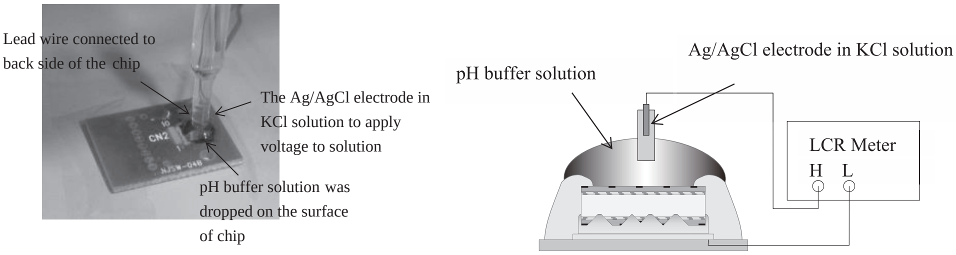
Outer circumference
was packaged by
adhesion bond

Fig. 3. Photograph of a fabricated device.

4. Experimental Results and Discussion

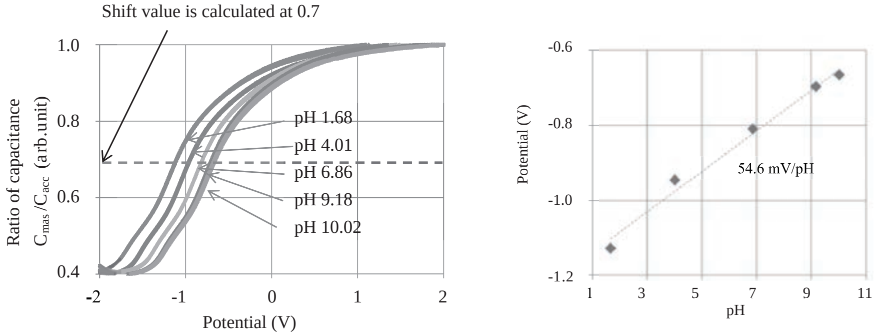
The pH sensitivity was measured by taking capacitance-voltage (CV) measurements with different pH buffer solutions. Figure 4 shows the experimental conditions for the CV measurements. Figure 4(a) shows a photograph of the setup, and Fig. 4(b) shows a schematic illustration of the measurement system. The CV measurements were carried out using an Agilent LCR meter operated at 100 Hz. A bias voltage was applied between the solution and the Si substrate. When the voltage applied to the solution was about −1.0 V above the threshold voltage, the silicon surface showed accumulation. Thus, the capacitance in accumulation was measured. In contrast, when the voltage applied to the solution was smaller than the threshold voltage, the surface showed inversion. Thus, the capacitance in inversion was measured. The threshold can be obtained from the ratio of these capacitances.(29) Using this technique, the pH sensitivity can be monitored by measuring the shift in threshold voltage.(30–32)

Figure 5(a) shows the results from the device without hydrogen annealing. The measurement results are shown by the ratio of the capacitance C_{mas} to the capacitance at a potential of 2 V, C_{acc},(31) where the device is in accumulation. The threshold voltage varies with the pH of the buffer solution. Figure 5(b) shows the relationship between pH and the shift in threshold voltage. The Si_3N_4 film had sufficient pH sensitivity, close



(a) (b)

Fig. 4. Experimental setup for CV measurements. (a) Photograph of device and (b) illustration showing CV measurement setup.



(a) (b)

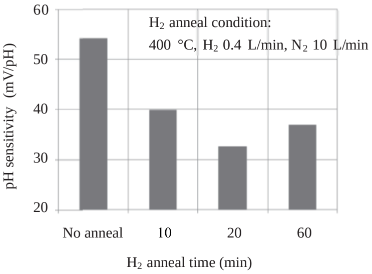
Fig. 5. CV measurement results showing variation in pH for device without hydrogen annealing.

to the ideal sensitivity given by the Nernst equation, to perform the hydrogen annealing experiments.

Figure 6 shows the variation in pH sensitivity with hydrogen annealing, which was carried out at 400 °C, with gas flows of H_2 at 0.4 L/min and N_2 at 10 L/min. The results show that with annealing, it was possible to reduce the pH sensitivity of the device to between 32.6 and 40.0 mV/pH. In these experiments, the pH sensitivity decreased and then increased at longer annealing times. The mechanism of the increase will be analyzed and discussed in our future work.

Figure 7 shows a comparison of the pH sensitivities obtained with annealing temperatures of 400 and 500 °C. In the CMOS-LSI process, the H_2 annealing temperature is not more than 550 °C, the temperature at which the Si-Al eutectic forms. The thermal energy was varied by selecting two different annealing temperatures. However, the pH sensitivity after annealing at 500 °C did not decrease much further, confirming that the annealing temperature was not a dominant factor in reducing this.

To find the region affected by hydrogen annealing, the surface of the Si_3N_4 film was lightly etched. After annealing for 20 min at 400 °C, the sample was etched in BHF solution. The pH sensitivity of the device is shown in Fig. 8. The sensitivity of the lightly etched device recovered to around the initial sensitivity given in Fig. 6. This result confirms that hydrogen annealing to decrease the pH sensitivity only affects the surface of the Si_3N_4, as expected.



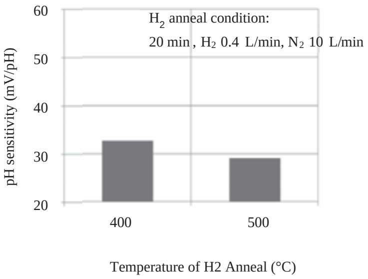


Fig. 6 (left). Experimental results for devices with and without H_2 annealing, showing variation in pH sensitivity with annealing time.

Fig. 7 (right). Comparison of pH sensitivity of devices with different annealing temperatures.

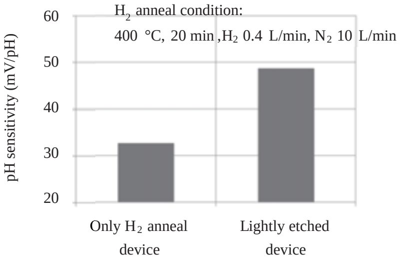


Fig. 8. Change in pH sensitivity of an annealed device after being lightly etched.

Experiments to establish whether the pH sensitivity could be decreased by H_2 annealing were performed and the result was confirmed. However, the resulting decrease in the pH sensitivity of the REFET was insufficient for this to be used in a pH sensor. Therefore, we will continue to perform further experiments in order to develop this type of advanced pH sensor.

5. Conclusions

We proposed a new method of decreasing the pH sensitivity of Si_3N_4 so that it could be used as the sensing membrane of a REFET, which is used as the reference electrode in a pH sensor. Experimental devices comprising Si_3N_4 on SiO_2 on n-type Si substrates were fabricated. The pH sensitivity of a chip annealed for 20 min in hydrogen at 400 °C was reduced from 54.6 to 32.6 mV/pH. Using a higher annealing temperature was ineffective in reducing this further. Annealing affected only the surface, not the interior of the Si_3N_4 film. We succeeded in developing the fabrication technology for a REFET device with low pH sensitivity.

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