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Novel pH Imaging Sensors based on CCD Technology.

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Introduction

If two dimensional distribution of various physical and chemical phenomena on real time with high resolution is obtained, a lot of unknown physical and chemical phenomena will be cleared. Needless to say, two dimensional distribution of visible, infrared, ultraviolet light and x-ray has been obtained by using commercial image sensors. Recently the several researches to obtain two dimensional distribution of physical and chemical phenomena have been carried out, for example the magnetic field distribution [1], the calcium ion distribution [2].

The measurement of physical and chemical reaction distribution is going to be remarkable to observe all sorts of phenomena. We notice the distribution of pH, because its measurement could make the metabolic activity of the microorganism and function of the neural cells clear. These phenomena occurred so quickly and subtly. In order to observe these reaction, the method to obtain the pH value on real time with high sensitivity is required. Moreover, a method to transfer the information of the pH distribution quickly is also required. The ISFET(ion-sensitive field effect transistor) is suitable for measuring pH value [3], then the theory of the ISFET will applied a sensor to obtain pH value. The CCD devices used in image sensors had made it possible to transform high speed signal to TV (television) picture. These two methods are alike in the way of fabrication, so it is possible to combine two devices. In this paper, we proposed a novel image sensor to observe the distribution of pH on real time and with high sensitivity.

The proposed CCD based pH imaging sensor has many advantages, such as high-resolution, high-speed (higher than TV-rate) etc. To observe a real-time transition of a distribution of the pH in a solution, a lot of unknown phenomena of the biology will be clarified, and the pH imaging sensor with high-resolution (less than 10μm) will observe the metabolic activity of microorganisms.

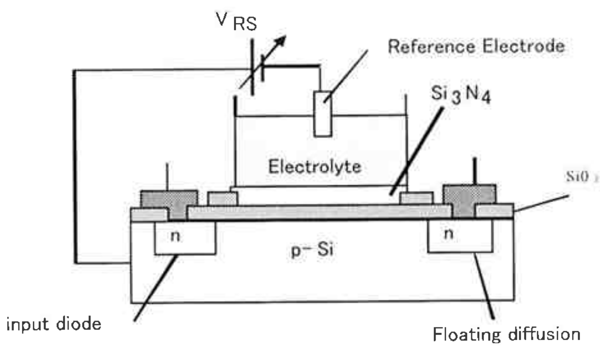

Fig.1 Schematic diagram of a pH measurement system.

Experimental & Result

A. pH sensing pixel

ISFET is one of the most useful pH point sensor. A pH sensing part of the proposed device consists of Si_3N_4 (hydrogen ion sensitive film) / SiO_2 / p-type Si substrate. The structure of the pH sensing part is almost same as the ISFET. However, the output signal of the proposed pH sensor is different from that of the ISFET. The output signal from the ISFET is the shift of the voltage between the gate and the source. On the other hand, the signal

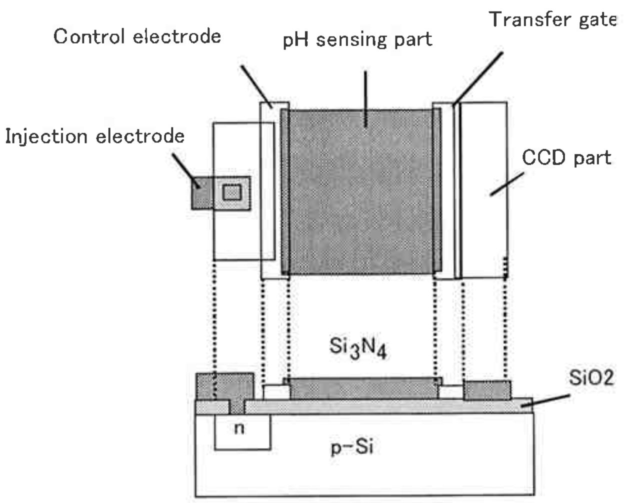

Fig.2 Schematic diagram of a pH sensing pixel.

from this device is the charges whose density varies according to the depth of the potential well under the pH sensing parts. This measurement system is shown as Fig.1. The reference electrode is inserted in the electrolyte to keep the potential of electrolyte constant. Reference electrode is biased at a voltage V_{RS}. As a pH value in a solution is varied, the amount of the hydrogen ions on the Si_3N_4 film is changed. Consequently, the potential on the Si_3N_4 film is shifted according to Nernst equation (theoretically, 59mV/pH at room temperature), and the depth of the potential well in the p-type Si under the sensing part is varied.

The schematic structure of a sensing part of the proposed pH imaging sensor is illustrated in Fig.2, and the potential well diagram is shown in Fig.3. A pH sensing part is constructed with $Si_3N_4/SiO_2/Si$ structure. The Si_3N_4 film acts as the hydrogen ion sensitive membrane. The potential well is formed in the Si substrate surface under the sensing part. As the density of hydrogen ions in a solution (i.e. the value of pH) is changed, the depth of the potential well is also changed. As the pH value on the sensing part becomes lower, the depth of this potential well is deeper. A sensing pixel has a sensing part and three electrodes; i.e. injection electrode, control gate, and transfer gate. The clock cycle is initiated by turning off the transfer gate (Fig.3 (a)). Next, the potential of the input diode decreases and electric charge is flowed into a potential well under a sensing part. The depth of the potential well is determined by the value of pH. The potential of a control electrode is fixed optionally, and is determined the lowest sensing value. If this potential was higher than the potential under sensing part, the charges could not be stored. A size of charge packet is created by potential difference between the control electrode and the sensing part, and the area of sensing part. The input diode is initially reverse biased over the control gate potential. Next, the input diode is briefly pulsed from V_{D1} to V_{D2} (Fig.3(b)) and kept again V_{D1} (Fig.3(c)). The well under the sensing part floods with charge and the excess charge beyond the control gate potential overflows to the input diode part. The charge corresponding to the pH value at the sensing part is remained in the charge packet. Lastly, the transfer gate is turned on, and the charge is transferred to the CCD part. The charges from each pixel of the pH imaging sensor are transferred and read out using the conventional CCD technique.

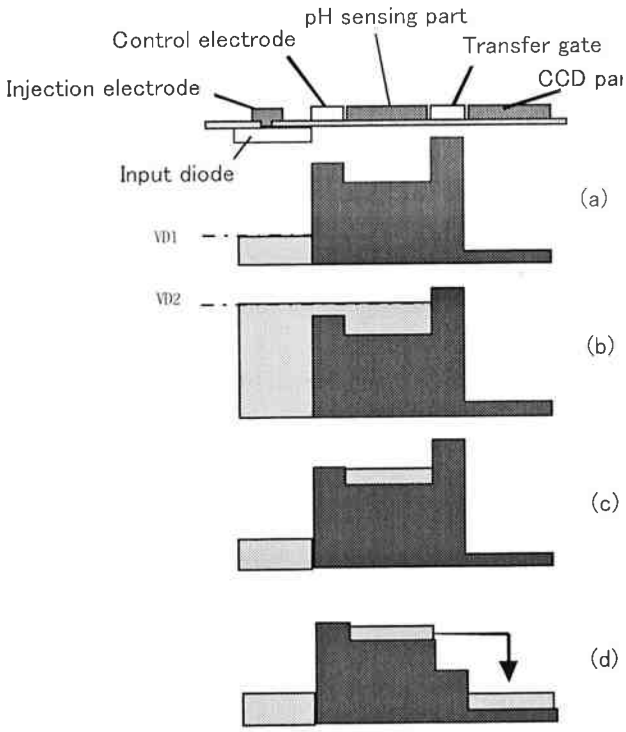

Fig.3 The principle of the conversion system from pH to charges.

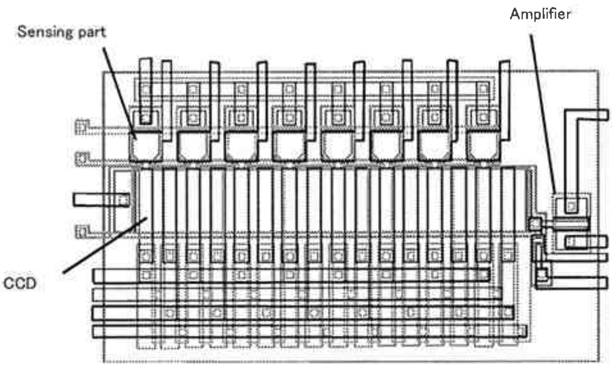

Fig.4 The design of the device. The device is constructed with 8 sensing pixels.

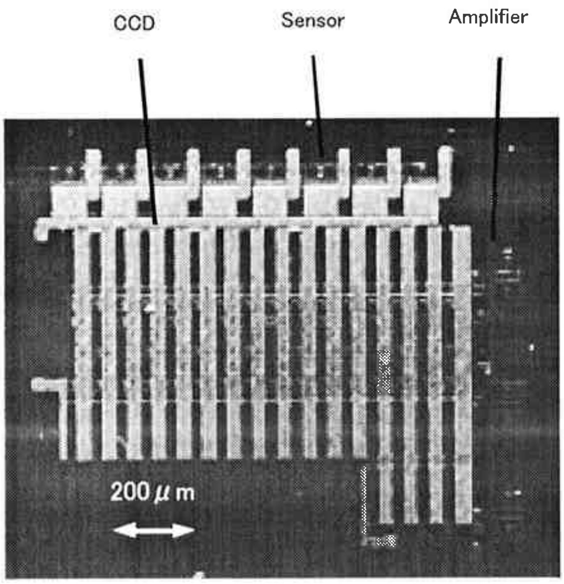

Fig.5 A photograph of the prototype CCD based pH image sensor.

B. Prototype pH image sensor

The prototype pH imaging sensor is fabricated using 20μm rule unrefined process. The thickness of the gate oxide (SiO_2) and hydrogen ion-sensitive membrane (Si_3N_4) is 50nm respectively. The device structure and the photograph are shown in Fig.4 and Fig.5, respectively. This test device has eight pixels, and is used typical four-phase CCD. The size of the sensing part is 100μm×100μm. The gate length and width of this CCD is 50μm and 200μm.

C. Results

The measurement of the device was carried out applying "equivalent voltages" to sensing parts instead of pH signals in electrolyte. The equivalent voltage was previously decided by using ISFET type pH sensor in the test element group. To use the ISFET, the change of the potential on the Si_3N_4 film is easily speculated. A result of the change of the potential on the Si_3N_4 film is shown in Fig.6 as a function of pH value of the standard solution. The potential on the Si_3N_4 film is linearly changed and this slope is about 50mV/pH. This results were utilized as equivalent voltage.

The output signal of a sensing part was measured by using the equivalent voltages. The equivalent voltage was applied by Al electrodes instead of the electrolyte in this measurement. The results is shown in Fig.7 as a function of pH value. It was found that the output signal from the imaging sensor was lineally changed from pH 0 to 14, and the total sensitivity was 45mV/pH from Fig.7. These value are strongly depended upon various parameters such as the area of floating diffusion, output transistor size. To optimize the output circuits, it is expected to distinguish less than 0.01pH. It is also found that the transformation efficiency (sensitivity) for chemical signal in the sensing part, whose size is 100□m square, was about 64000electrons/pH.

Using the prototype pH image sensor, we successfully observed a pH image as shown in Fig.8, which is demonstrated on a black & white TV

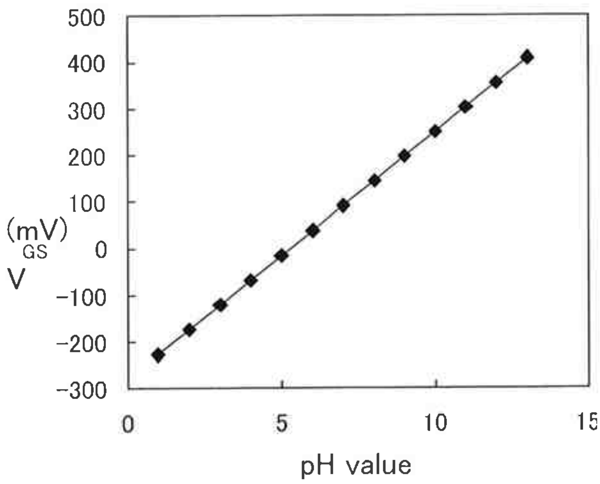

Fig.6 Sensitivity of activated sensor for $Si_3N_4/SiO_2/Si$ structure to pH.

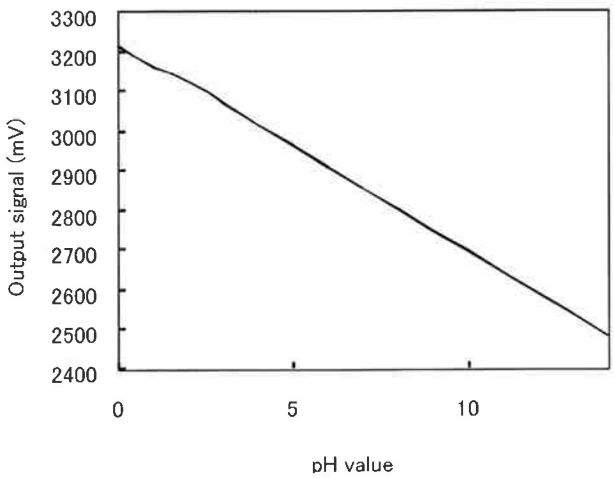

Fig.7 Output signal from the fabricated prototype image sensor as a function of equivalent pH values.

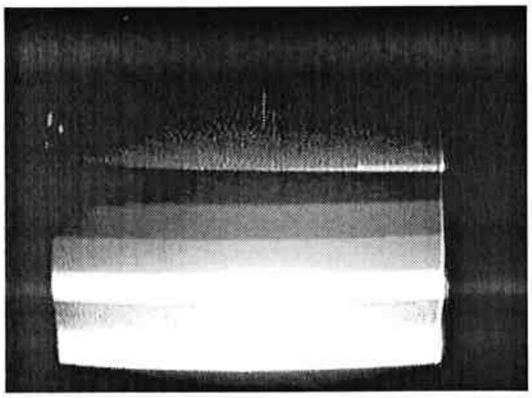

Fig.8 TV picture of 8 pixels applied different equivalent voltages one another.

monitor. The operation frequency was 2KHz. It was found that each pixel is different brightness on the monitor to add different equivalent voltages, which indicated from pH 4 to 12, to sensing parts respectively.

Conclusion

We proposed and demonstrated a novel pH imaging sensor based on the CCD technology. This device consists of pH sensing parts, conventional CCD parts and read out circuit. A thin Si_3N_4 film which acts as the proton-sensitive membrane was used in the pH sensing film. The prototype devices were fabricated using 20μm rule unrefined process. This prototype device has eight pixels, and is used typical 4-phase CCD. The output signal from the imaging sensor was lineally changed from pH 0 to 14, and successfully observed a pH image on a black & white TV monitor.

The pixel size of the pH sensitive area was relatively large. However, we believe that the pixel size of the imaging sensor can be decreased less than 5μm×5μm by using refined fabrication equipment. This initial work shows the possibility of observation of a real-time transition of a distribution of the pH in a solution and paves the way for high-resolution pH imaging sensors

References

1) Nixon O and Arokia Nathan, Technical Digest of IEDM, p.167, (1995).

2) S.-Y. Hua, M. Nohmi, K. Kuba,. *J.Physiol.*, 464, p245 (1993)

3) P.Bergveld, *IEEE Trans. Biomed. Eng., BME-17*, 70 (1970)