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ELECTROCHEMICAL REFERENCE ELECTRODE FOR THE ION-SELECTIVE FIELD EFFECT TRANSISTOR

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By means of the monolithic integrated circuit techniques with the plasma polymerization method, a reference field effect transistor (REFET) has been developed to be used with the ion-selective field effect transistors (ISFET's). The gate insulator of the REFET is coated with a plasma polymerized styrene film. It was used in combination with the pH-ISFET to determine pH values. Experimental results compared favorably with those from the convetional glass electrode method.

The ISFET, developed from the fabrication techniques of semiconductor devices, is one of the most important chemical sensory devices used in potentiometric applications in the chemical, biochemical and medical fields. It is especially advantageous because of its extremely small size, solid-state structure, in situ impedance conversion and the ability to fabricate multi-ion sensors. The theory and mode of operation of the ISFET's have previously been reviewed and reported on by several advanced researchers.[1-13] Reliable and suitable reference electrodes are prerequisites for the operation of ISFET, as found in conventional ion-selective electrodes (ISE's). The quality of potentiometric measurements depends on the performance of both the ISFET and the reference electrode. Namely, it is imperative to obtain a suitable reference electrode of the same size as or smaller than that of the ISFET's.

As a result, a micro-size and solid-state reference electrode has been fabricated to be used in combination with the ISFET. This REFET has a schematic configuration as shown in Figure 1, that is, the gate insulator of the ISFET is directly coated with the plasma polymerized styrene thin film. This film prevents the variations of the interface potential, which is located between the gate insulator and electrolyte, from being adversely affected by the species and activities of ions being dissolved in sample solutions.

The basic pH-ISFET chips with the ditantalum pentaoxide gate insulator were fabricated following the MATSUO process.[7] All of the chips used in these experiments were examined and normal pH-response characteristics were confirmed. Eight ISFET chips were then set in a reactor chamber (its volume was ca. 0.13 m^3) of a plasma glow-discharge apparatus having an internal electrode and a flowing gas system.[14] Two glow-discharge electrodes (silver plates: each 5 $\times$ 5 cm, 0.3 cm thick) were installed parallel to each other in the center of the reactor chamber

2.5 cm apart and eight chips were fixed on the inside surface of one of the discharge electrodes. The pressure of chamber was kept in a vacuum of 0.01 Pa for one hour. Styrene monomer vapor was then introduced into the chamber at the flow rate of 25 cm^3 min^{-1} for an hour in order to clean the electrode surfaces and chips. The glow-discharge conditions were as follows: atmosphere, styrene monomer vapor of 133 Pa ; electric power, ca. 8 W (9.8 kHz) ; temperature, 25°C ± 1°C, period of glow-discharge time, 30 s ; thickness of polystyrene film, ca. 0.4 μm estimated. Following the glow-discharge, the flow of styrene monomer vapor was discontinued and chamber with the ISFET chips was left in the vapor of which pressure was kept at 133 Pa for 24 hours. The coated chips were taken from the chamber and immersed in an aqueous solution of 0.1 mol dm^{-3} potassium chloride at 22°C ± 1°C for a week. The REFET dimensions were 6.5 mm long, 0.5 mm wide and 0.23 mm thick. The sensory portion of the chip was ca. 0.6 mm long on the tip.

Five pairs of REFET and pH-ISFET were prepared to evaluate the performance and to confirm reproducibility. Each pair was installed successively in a differential mode instrument as shown in Figure 1 and the pH response was tested. Each pair responded with same general characteristics, representative data of which are shown in Figure 2. In addition to the tested pairs of electrodes, the conventional

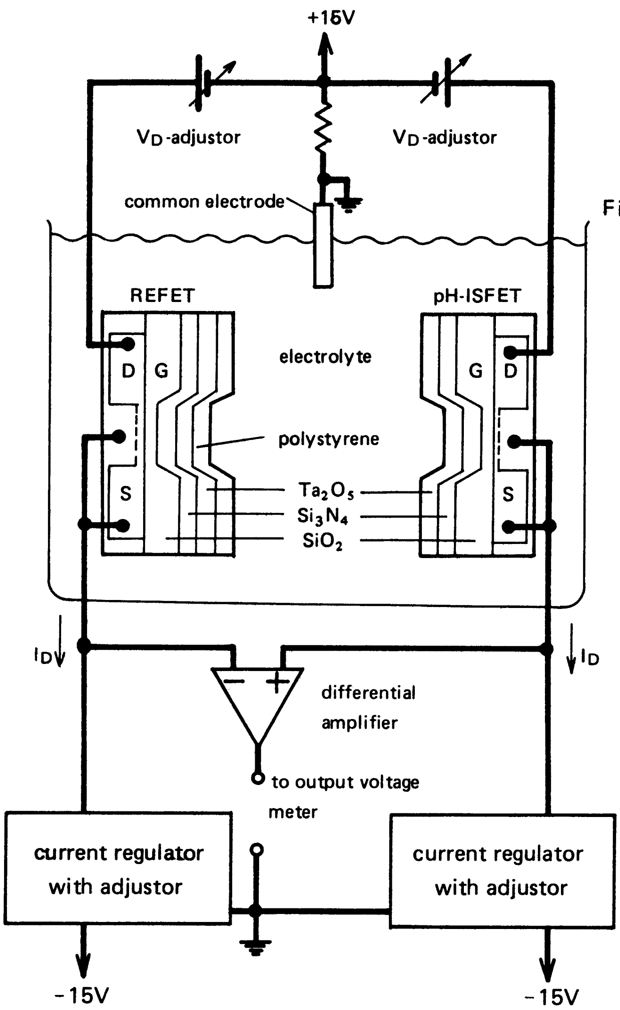

Fig. 1 Schematic configuration of the present REFET and the circuit diagram for pH measurement with the pH-ISFET and REFET.

Generally, in the normal operation of the FET, I_D is measured as the function of V_{GS}. In this circuitry, however, it should be noted that V_S is measured as the function of V_G during which the I_D is kept constant by means of the current regulator, because V_S answers directly to the V_G. Thus the output voltage meter of the differential amplifier indicates the potential difference between the gates of the pH-ISFET and REFET.

D: drain, G: gate, S: source,
I_D : drain current, V_D : drain voltage,
V_G : gate voltage, V_S : source voltage,
V_{GS} : gate-source voltage.

glass electrode system (used as a reference method in this experiment) were put in the test solution for pH determination. The satisfactory conformities of pH values obtained in the present method and in the reference method ranged between pH 2-12, as shown in curve (a). Although an exact measurement is not possible, the results show that the REFET remains stable against pH variations as shown in curve (b). Curve (b) represents the data plotted from the output signal of the tested REFET to pH values using the conventional reference electrode (silver-silver chloride electrode with 0.1 mol dm^{-3} potassium chloride solution) as a contact between the solution and the transistor substrate. Clinical application of direct pH determination of blood serum is the primary motive of the present investigation. It was confirmed in the above-mentioned methods that there was no interference with the pH determination, when tested with 30 other species of inorganic ions (e.g. Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, HCO_3^- and HPO_4^{2-}) and 20 organic chemicals or matrices (e.g. proteins, enzymes, hormones, sugars, lipids, vitamines and nitrogen compounds) all of which are generally present in blood serum. The chemicals used in these experiments were of analytical reagent grade. The pH-meter with glass electrode system was calibrated in accordance with the Japanese Industrial Standard (JIS Z 8802). According to the scanning electron microscopic observation, it was found that the surface of the polystyrene film was dotted with many small particles of plasma polymerized styrene. The lower layer of the polystyrene was tightly constructed and without pinholes. The special structure of the film shows that potassium chloride solution is held tightly on the surface of the film and is never in contact with ditantalum pentaoxide layer. It seems that the held solution works as a kind of salt bridge and that the REFET keeps constant potential even if it is immersed in any kind of solution.

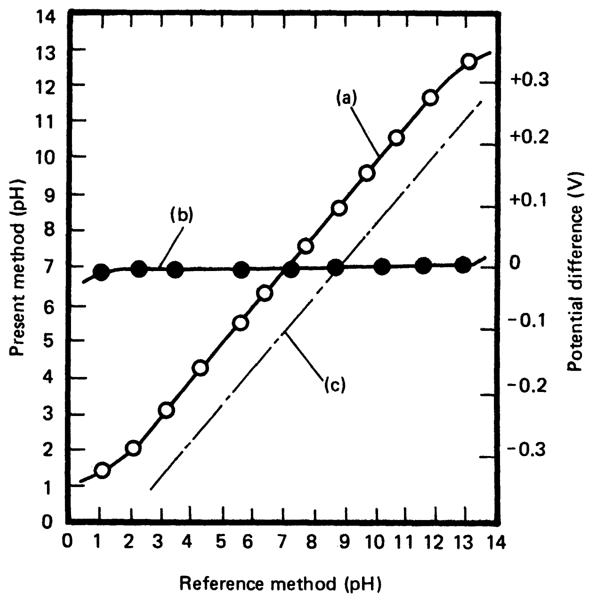

Fig. 2 The pH response of the present method (a) and the stability of the REFET (b)

A conventional pH-meter with the glass-Ag/AgCl (0.1 mol dm^{-3}-KCl) electrodes was used as a reference method.
The test solution was a mixture of 0.1 mol dm^{-3}-HCl and 0.1 mol dm^{-3}-NaOH.
A conventional Ag/AgCl (0.1 mol dm^{-3}-KCl) electrode was used as a solution contact in curve (b).
The initial points of measurement were adjusted by means of an electronic adjustor.
Curve (c) is the theoretical Nernstian slope.

Since the durability and strength of electrodes are prerequisite for longer life reliability, more experimental works have to be conducted not only from the present standpoint, but also from others using different parameters. Such preliminary experimental results have revealed the possibility of creating a suitable micro-reference electrode to be used with the ISFET. Although the REFET's were fabricated on a separate chip from the pH-ISFET chip, at the present time, a monolithic configuration in which the REFET gate and pH-ISFET gate are combined on a single chip will offer more efficient results. With the characteristics of the two transistors perfectly matched, the noise levels will be greatly improved. Furthermore, when the polystyrene film is directly coated on the trisilicon tetranitride layer, the ditantalum pentaoxide layer may be excluded in the case of the REFET. Further experiments will enlarge the applications and feasibility of this technique.

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