

Fabrication of Smart Electrochemical Sensor with CMOS Integrated Circuits

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1. Introduction

Currently, electrochemical measurements have attracted significant attention due to its promising application in battery industries, bio-sensing and environmental assessment.

General electrochemical analyzer tends to become smaller and more portable recently, and smaller electrochemical measurement system assembled by discrete operational amplifiers (OPAMPs) and resistances has also been reported [1]. A recent article report on electrochemical sensors to detect DNA hybridization with CMOS based circuits [2], in which only working electrodes are fully internal, and an external reference electrode and counter electrodes are adopted. If both circuit systems and sensor units are integrated within a single chip in the true sense, it could be the smallest electrochemical system.

Electrochemical analyzer is generally rather expensive and it is still difficult to measure dozens of points at the same time. A smart sensor, in which both sensor electrodes and drive and read-out circuits are integrated, would make low cost and multi-point measurement possible. One of our goal is to realize electrochemical measurement system using all-in-one chip. Our group previously reported an observation of hybridization of DNA using nMOSFET based OPAMPs [3].

In this article, we report the fabrication of a smart electrochemical sensor chip in the integration of a working electrode, a counter electrode, and CMOS OPAMPs working as a potentiostat and report evaluation of this smart sensor chip from the point of electrochemical reaction especially cyclic voltammetry. By using CMOS FETs constructing an OPAMP, a number of FETs has decreased to less than half from that of nMOS configuration [3].

2. Sample Fabrication

Signal processing circuits were fabricated based on 5 μm CMOS process. OPAMPs were constructed of CMOS-FETs. After circuit fabrication, sensor electrodes of a gold working electrode (WE, 1.6 mm in diameter) and a platinum counter electrode (CE, 8.3 mm² in area) were fabricated on the same chip. A top view of the chip and magnified area of OPAMPs are illustrated in Fig. 1(a) and (b). Reference electrode was off chip.

The diced chip (25 mm²) was bonded on a 80-pin-package, connected through gold wires and adhesive was put on the periphery of the chip, as shown in Fig.2. To

drive potentiostat, DC voltage supply was connected through the package.

3. Experimental and Results

Evaluation of OPAMPs

To realize a function as a potentiostat, CMOS based OPAMPs were fabricated on a chip. Fig. 3. exhibits a basic property of an integrated OPAMP working as voltage follower. A potentiostat mainly consists of two OPAMPs. The OPAMPs work as a drive circuit and a read out circuit respectively, as shown in Fig. 4. The resistance R1 is used to stabilize OPAMP1 because CE has large area (8.3 mm²) and larger capacitive load which sometimes causes an oscillation. The OPAMP2 and R2 works as a current-voltage converter. A voltage between RE and WE are adjusted through potentiostat.

Electrochemical Measurement

Ferrocyanide water solution (10.0 mM) was prepared to check sensor chip from the point of electrochemical reaction. A reduction oxidation reaction of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ were measured. The sample solution amount of 70 μl was put on the chip.

Cyclic voltammetry is a typical measurement technique, to drive the reduction-oxidation reaction through sweeping a potential. The potential starts from -100 mV (versus a standard Ag/AgCl 3M NaCl reference electrode) to the +600 mV and swept back to -100 mV at various sweep rate.

Because of integration of a potentiostat in a chip, it was possible to measure cyclic voltammetry without using special electrochemical analyzer. The sweep rate was changed from 10 to 100 mV/s. Clear oxidation and reduction peaks were observed as shown in Fig. 5. The peak positions were almost the same as the peaks acquired through general electrochemical analyzer (CV-50W, BAS). Heights of reduction-oxidation current peaks increased as sweep rate became faster. Redox current vs. square root of sweep rate was plotted in Fig. 6. The linear relationship was in agreement of theoretical behavior. It is confirmed that a measurement of electrochemical signal is possible using integrated systems based on CMOS-FETs.

4. Conclusions

We have fabricated a microchip in which both sensor electrodes and CMOS based signal processing circuits were

integrated. By using CMOS FETs as signal processing circuits, the number of FETs has decreased to less than half from that of nMOS configuration [3]. Clear electrochemical signals through cyclic voltammetry were acquired and confirmed by comparing data using general electrochemical analyzer.

This result sheds light on a possibility of realization of a really smart electrochemical sensor with the integration of various CMOS circuits including ADC, shift registers and signal generators.

Acknowledgements

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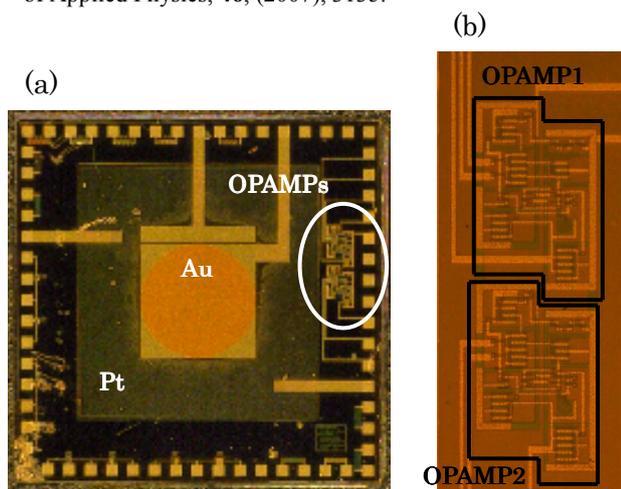


Fig. 1 (a): Top view of reduction oxidation sensor chip with signal processing units integrated. (b): magnified picture of OPAMPs of CMOSFET composition.

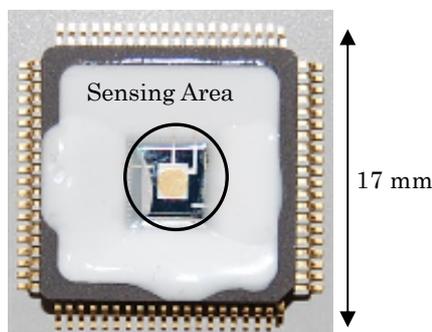


Fig. 2 A picture of a sensor chip set on a package. Adhesive was put on the periphery of the chip.

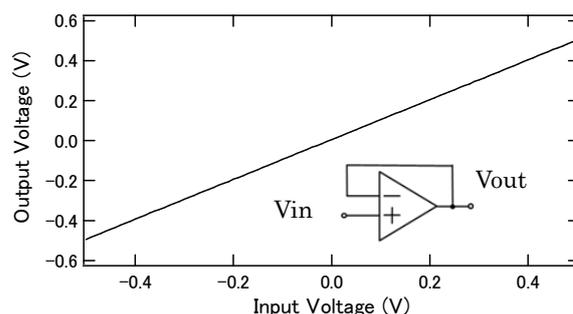


Fig. 3 Basic CMOSFET based OPAMP characteristics.

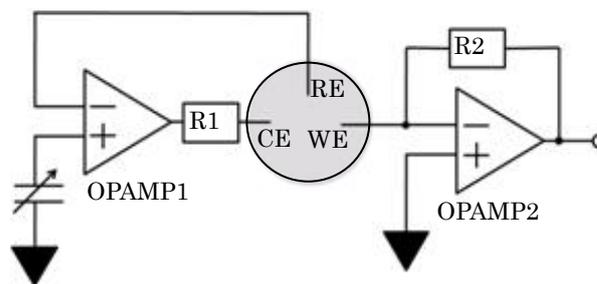


Fig. 4 A potentiostat which consists of two OPAMPs integrated on a chip.

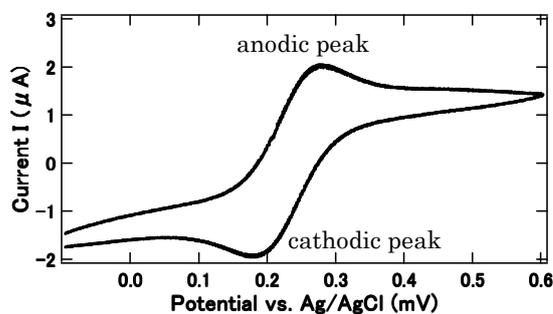


Fig. 5 Typical cyclic voltammetry acquired using a sensor chip in which circuits are integrated. Scan rate was 10 mV/s. Sample solution was 10.0 mM $K_3[Fe(CN)_6]$ water solution.

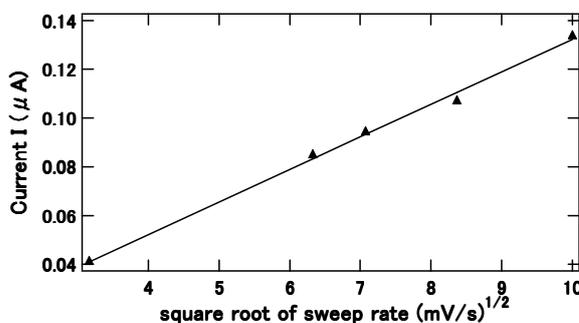


Fig. 6 Square root of sweep rate versus anodic peak current. Correlation coefficient is 0.9938.