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Highly sensitive palladium oxide thin film extended gate FETs as pH sensor

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ABSTRACT

It is well-known that palladium readily absorbs hydrogen gas at room temperature. Based on this unique property of palladium, palladium oxide (PdO)-sensitive membrane in the extended gate field-effect transistor (EGFET) configurations have been evaluated as a detector for hydrogen ions in pH buffer solutions. The PdO thin film was prepared by a two-step process through reactive electron beam evaporation and subsequent thermal oxidation in an optimal O_2 flow. Our results indicate that the PdO-based EGFET sensor showed super-Nernstian sensitivity approximately 62.87 mV/pH, while exhibiting good linearity as well as good stability between pH 2 and pH 12. Our research demonstrates that PdO membrane can be used in EGFET structure without compromising sensitivity achieved by conventional methods. Furthermore, the disposable PdO sensor shows great potential for low cost biochemical detection due to its simplified fabrication and measurement system.

1. Introduction

The detection of ions and molecules in a biochemical environment plays a significant role in chemical science and biotechnological application. The basis of an ion-sensitive field-effect transistor (ISFET) is derived from a metal-oxide semiconductor field-effect transistor (MOSFET), of which the metal gate is hereby substituted by an ion-sensitive membrane with direct contact with a buffer solution [1]. Since the invention of the first ISFET by Bergveld in 1970 [2], various techniques and sensing membranes have been exploited. The potential of these solid-state devices have attracted a great deal of attention, due to their numerous advantages such as miniaturization, chip-circuit design and low cost in manufacturing. In particular, they are an excellent candidate for the integration of biochemical sensors in microelectronics. Several ISFET-based biochemical sensors have been proposed [3,4]. However, owing to the fragile nature of membrane degradation in extreme conditions, extended gate field-effect transistor (EGFET) configuration has been developed to prolong stable operation. The mechanism of surface ion adsorption in ISFET and EGFET are essentially the same, with the major difference that EGFET configuration can only be used in low impedance membranes. EGFET is a subset of the ISFET family line, which modifies the ISFET into a two-part design. The sensing membrane is immersed in the solution, while connected to a remote FET IC chip for real-time analysis [1,5,6]. This approach enables us to swap the sensing membrane from any chemical damage instead of fabricating a whole new device.

Prompted by the demand for low cost chemical sensors, researchers looked into SiO_2 initially for pH sensitive membrane. The search for a more compatible material continued as sensitivity and stability impacted the performance of these chips. Since the realization of Ta_2O_5 as a pH-sensing membrane in 1981 by Matsuo et al. [7], various research groups have demonstrated the use of different sensing membranes such as Al_2O_3 [8], Si_3N_4 [4], SnO_2 [9], Er_2O_3 [10], Si nanowire/SiO_2/Al_2O_3 [11], IrO_X [12], Gd_2O_3/SiO_2 stacked oxide [13], silicon nanowire [14], Ru-doped TiO_2 [15] film in order to enhance detection capabilities. As the Nernst limit of pH sensitivity is 59 mV/pH, "super-Nernstian" sensitivity >59 mV/pH could promise a far more precise detection in monitoring the pH levels in blood and extracellular fluids.

In the 1980s, both Grubb and King [16] and Liu et al. [17] demonstrated the use of palladium–palladium oxide as a wire form electrode for their sensor fabrication. Both fabricated sensors revealed merits in pH detection, with the exception reported by

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Liu et al., for exceeding Nernstian behavior with 71.4 ± 5 mV/pH. Grubb and King employed high temperature thermal oxidation of the palladium wire, whereas Liu et al. used electrochemical anodization. This was followed by the works of Kinoshita et al. [18] and Bloor et al. [19], whose groups also fabricated Pd–PdO pH electrode via thermal oxidation and electrochemical route respectively. Then in 1986, Karagounis et al. [20] demonstrated the possibility of fabricating Pd–Pdo thin film potentiometric pH sensor through RF reactive sputtering technique, reaching a pH sensitivity of 54 mV/pH in the pH range between 3 and 9.

Despite the promising developments in biochemical sensors, Pd–PdO-based sensors in EGFET configurations have not yet been reported. Therefore in this investigation, we propose a highly sensitive membrane consisting of PdO thin film as a pH sensor in the EGFET format. The sensor's performances in sensitivity, stability and reversibility were measured and analyzed. The experimental results have demonstrated that super-Nernstian pH response was reached with similar sensitivities achieved by conventional methods. These findings demonstrate a novel and effective design of a biochemical sensor by unifying the compound semiconductor sensing membrane with the silicon integrated chip technology.

2. Experimental details

2.1. PdO film preparation

Extended gate field-effect transistors, comprised of PdO thin film sensing membranes were fabricated on sapphire substrate and encapsulated on a copper clad FR-4 printed circuit board (PCB) laminate sheet. To begin with, 130 nm thickness of palladium oxide film was deposited by reactive electron beam (E-Beam) evaporation from a 99.999% pure Pd slug on a two inch sapphire substrate under O_2 flow of 20 sccm. The PdO thin film on sapphire then underwent an annealing in furnace at 973 K for an hour in O_2 flow of 1 slm. The two-step process was employed for the enhanced formation of PdO film. Morphology analysis was done using field emission scanning electron microscopy (FE-SEM). In addition, X-ray photoelectron spectroscopy (XPS) study was employed to characterize palladium–oxygen species on the surface of PdO film. Analysis through Hall measurement revealed the p-type semiconductive nature of PdO film with sheet resistivity, sheet carrier concentration and mobility of about 1221 Ω/□, $5.93 \times 10^{14}\ \mathrm{cm^{-2}}$ and $8.61\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ respectively.

2.2. PdO sensor chip fabrication

Copper Clad FR-4 – PCB laminate sheet was first etched to fabricate a mounting template for the sensor chip as shown in Fig. 1(a). Samples of $1 \times 1\ \mathrm{cm^2}$ size were scribed from the native wafer for sensor chip fabrication. For pH detection studies, $1 \times 1\ \mathrm{cm^2}$ PdO/sapphire sample was mounted on square shaped area and bonded via silver paste. Silver paste was then applied carefully in the surrounding edges of the PdO layer and extended to copper plate, as to form the conductive line between sensing membrane and PCB. A homemade epoxy package was employed to encapsulate sensor chip and copper line while exposing a sensing area of approximately $0.25\ \mathrm{cm^2}$ free from epoxy. The completed sensor as shown in Fig. 1(b) chip was immersed in pH 7 buffer solution for 24 h, allowing sensing surface to stabilize prior to current–voltage (*I–V*) measurement. A Texas Instruments n-MOSFET CD4007UBE was used as the FET in the EGFET device. The dimension n-MOSFET used for our measurement consists of gate length and gate width of 10 μm and 30 μm, respectively. We have used signal line of coaxial cable to connect copper metal line of fabricated PdO sensor chip and the gate of n-MOSFET as shown in Fig. 1(c). Fig. 1(d) shows the schematic diagram of completed PdO pH sensor chip.

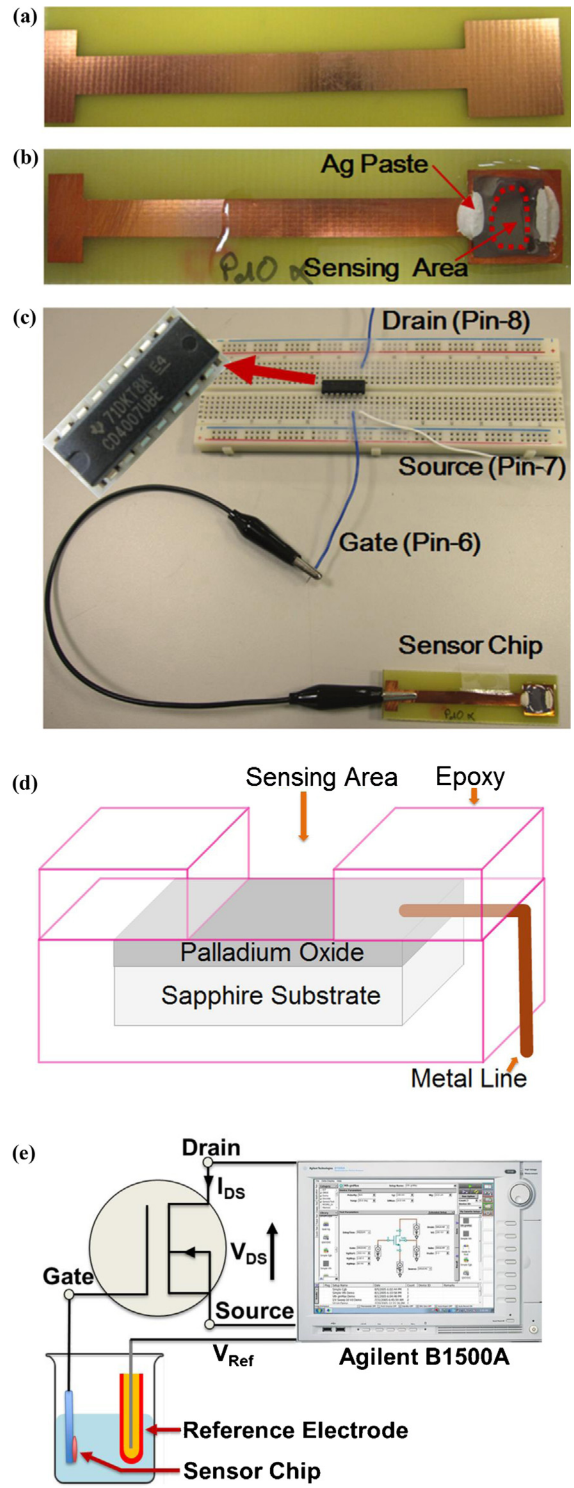

Fig. 1. Photograph of (a) bare PCB mounting template, (b) encapsulated PdO sensor chip and (c) final PdO sensor chip connected to the gate of n-MOSFET; schematic illustration of the (d) fabricated PdO sensor chip and (e) *I*–V measurement setup for the PdO pH-EGFET sensor.

2.3. Measurement of sensor chip

All current–voltage measurements took place in a shielding box in order to prevent any light exposure or electromagnetic