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Review

Preparation and characteristics of ruthenium dioxide for pH array sensors with real-time measurement system

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Abstract

Ruthenium oxide (RuO_2) thin film was used as the sensing layer of hydrogen ion selective electrodes (ISE) for pH array sensors. The RuO_2 sensing membrane was deposited onto a silicon wafer substrate using radio frequency sputtering technology. We measured the I_{DS}–V_G curves of the RuO_2 sensing membranes connected to a MOSFET with conducting wire and immersed in the pH buffer solutions at different pH concentrations using a Keithley 236 Instrument. The results obtained the pH sensitivity of the RuO_2 sensing membrane for the ISE devices at about 55.64 mV/pH. From the nonideal characteristic experimental results, the drift rate of the RuO_2 ISE device was obtained at 0.38 mV/h at pH 7. The hysteretic widths of the RuO_2 ISE device were 4.36 mV and 2.2 mV in pH 7–4–7–10–7 and pH 7–10–7–4–7 loop cycles, respectively. The RuO_2 ISE was used for the pH array sensors structure to reduce the measurement error and testing time for four single sensors. And the reproducibility, stability, selectivity and response time of RuO_2 array sensors were investigated. A real-time measurement system for pH array sensors was achieved. The system has the following advantages: portable USB DAQ card, easy to setup and use, with an application program development by the Visual Basic software, which is easily used in other computers.

Keywords: Ruthenium oxide; Ion selective electrode (ISE); pH array sensors; USB data acquisition; Real-time measurement system

Contents

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1. Introduction

Conventional pH electrodes are usually based on a pH selective glass membrane. Many conductive oxides, instead of a noble metal, are used to fabricate the electrode material. It should be possible to form a well-oxidized homogeneous coating onto a substrate surface. Fog and Buck [1] reported a number of metal oxides including RuO_2, PtO_2, TiO_2, OsO_2, IrO_2, RhO_2, Ta_2O_5, and SnO_2 produced from metal powders or oxidized metal. The pH-measured value is an important parameter for different application fields including clinical diagnosis, high pollution environment monitoring, and industrial wastewater measurement. The first material used as a pH-sensitive dielectric for the ion sensitive field effect transistor (ISFET) was silicon dioxide (SiO_2) introduced by Bergveld [2] in 1970. However, there were still drawbacks in the ISFET sensing structure that needed to be improved, such as the poor isolation between the devices and the chemical solutions, and the sensitivity optical effects. The ISFET device was formed directly onto the FET gate electrode. Its chemical and biological applications are limited by its structure. The disadvantages in the ISFET structure affect the device stability in the measurement process. These disadvantages can be improved by using the ion selective electrode (ISE). The ISE is another approach for isolating an FET. The sensing membrane is deposited at the end of a conducting wire that extends from the FET gate area. There are some advantages in using the ISE structure, such as the light insensitivity, simple to passive and package the sensing devices and flexibility in shaping the extended gate area. A variety of deposition techniques using radio frequency sputtering [3–6], pulsed-laser deposition (PLD) [7], sol gel [8], and chemical vapor deposition [9–11] have been employed to synthesize RuO_2 thin films.

The ISFET array sensors were used as an on-line water pollution monitoring system [12]. This system included a smart ISFET array that detects different ion concentrations in real-time. Tin oxide (SnO_2) films are used as the sensing membrane for fabricating array sensors combined with a real-time sensing system [13]. An array sensing system using single sensor will reduce the measurement errors and testing time.

Ruthenium dioxide (RuO_2) thin films were prepared in this study using the RF sputtering system from a ruthenium target deposited onto a silicon substrate [4]. The sensitivity, pH measurement range and the nonideal RuO_2 sensing membrane characteristics are investigated. We adopted four RuO_2 sensing membrane ISE devices to form array sensors to reduce the measurement error and produce a real-time measurement system to reduce the testing time. Visual Basic 6.0 software was used to design the window graphic user interface (GUI) measurement operation interface for the real-time measurement system.

2. Experiment

2.1. Reagents and materials

Silicon wafers were used as the substrate for the ruthenium dioxide sensing membrane. The silicon substrate was p-type, (1 0 0)-oriented, resistivity 15–25 Ω-cm, and supported by the National Nano Device Laboratories (NDL). The RuO_2 sensing membrane was prepared using a sputtering process. The RuO_2 thin film was deposited onto the silicon substrate maintained at 25 °C using radio frequency sputtering from a 2 in.-diameter, 1/4 in.-thickness, and 99.99% purity ruthenium metal target. Acetone and methanol solvents were purchased and used for cleaning the silicon wafer.

2.2. Fabrication of the RuO_2 sensing membrane

The silicon substrates were cleaned ultrasonically in acetone and methanol alternately for 15 min, leached in distilled water, and then dried. In this experiment the RuO_2 pH-sensing membrane was prepared using the R.F. sputtering system. The sputtering operating pressure was 10 mTorr in Ar gas mixed with O_2 for 1 h. The gas flow ratio of the Ar:O_2 was 4:1. The silicon was then cut into squares 0.5 cm × 0.5 cm in size and packaged with epoxy resin. The radio frequency power was 100 W, at 13.56 MHz (Model: SKN-05P, Japan). A schematic diagram of the RuO_2 thin film sputtering system is shown in Fig. 1. The RuO_2 ISE pH sensor was separated into two parts: the sensing membrane and the MOSFET structure. The RuO_2 membrane was used as the sensor head and encased in epoxy, leaving a

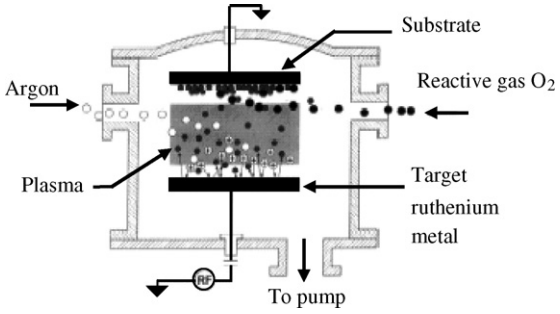

Fig. 1. Schematic diagram of the sputtering system for the RuO_2 thin film.