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The effects of sensing electrode thickness on ruthenium oxide thin-film pH sensor

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ABSTRACT

A miniaturised pH sensor structure employing an R.F. sputtered ruthenium oxide sensing thin-film electrode in conjunction with an electroplated Ag/AgCl reference electrode is developed and the effect of the thickness of the sensing electrode on the measurement accuracy is investigated. Experimental results show that the pH sensor exhibits Nernstian slopes of 66.52 mV/pH, 68.63 mV/pH, 67.73 mV/pH, and 54.83 mV/pH for ruthenium oxide film thicknesses of 425, 300, 175 and 50 nm, respectively. All the pH measurements were carried out at a temperature of 22 °C. The performance and characterisation of the pH sensors in terms of sensitivity, response time, pH resolution, stability and reversibility are discussed.

1. Introduction

pH sensors are widely used in chemical and biological applications, such as water quality monitoring, blood monitoring, chemical and biological analyses, environmental monitoring and various clinical tests [1], where pH measurements are vital for the characterisation of aqueous solutions. In biomedical applications, in particular, both, the solubility of chemicals or biomolecules and the rate of chemical reactions are dependent on the pH level; therefore, monitoring the pH level is crucial for preventing unwanted, and sometimes harmful, reactions. In addition, measuring the pH value of water sources such as rivers, lakes and oceans is one of the most important analytical methods adopted by laboratories and industry for monitoring the water quality neutralising treated industrial waste water. The most widely used technique for pH measurement is based on the use of conventional glass pH electrodes [2,3]. While the performance of glass electrodes is excellent in terms of high sensitivity, long-term stability, high ion selectivity and wide operating range, such electrodes have many disadvantages including mechanical fragility, need for wet storage, large size, limited shape and high cost.

Various metal oxides such as RuO_2, IrO_2, PtO_2, RhO_2, TiO_2, SnO_2 and Ta_2O_5 have recently been investigated for realising pH sensing electrodes due to many attractive features including insolubility, stability, mechanical strength, electro-catalyst and manufacturing technology [4–6]. Ruthenium oxide, particularly, exhibits unique advantages in comparison with other metal oxides, including thermal stability, excellent corrosion resistance, low hysteresis high sensitivity, and low resistivity. pH sensors employing thick film ruthenium oxide pH sensing electrodes, developed using screen-printing technology, in combination with standard electrolyte-filled Ag/AgCl reference electrodes have recently been demonstrated [7,8]. While screen printing is a cost-effective deposition technique for thick film development, it is impractical for the development of sub-micron thin-films. Recently, pH sensor structures based on the use of sub-micron RuO_2 thin films have been reported [9–11]. However, such pH sensor structures were not optimised since the effect of the thickness of the ruthenium oxide thin-film electrode on the sensor performance was not extensively investigated.

In this paper, we thoroughly investigate the effect of the thickness of the RuO_2 thin-film on the performance of pH sensors employing a sub-micron thin-film RuO_2 sensing electrode developed using reactive R.F. magnetron sputtering in conjunction with an electroplated Ag/AgCl reference electrode. Experimental results show that the optimised pH sensor offers several advantages such as miniaturisation, ease of packaging, low cost through the use of micro fabrication processes, ruggedness, disposability and capability of measuring pH at high temperatures [11]. RuO_2 thin film thicknesses of 50 nm, 175 nm and 300 nm are tested using standard pH buffer solutions of pH 4, pH 7 and pH 10 which typically validate acidity and alkaline behaviour for commercial pH sensors calibration. However, the developed sensor typically operates over a wider pH range (pH 2–pH 12).

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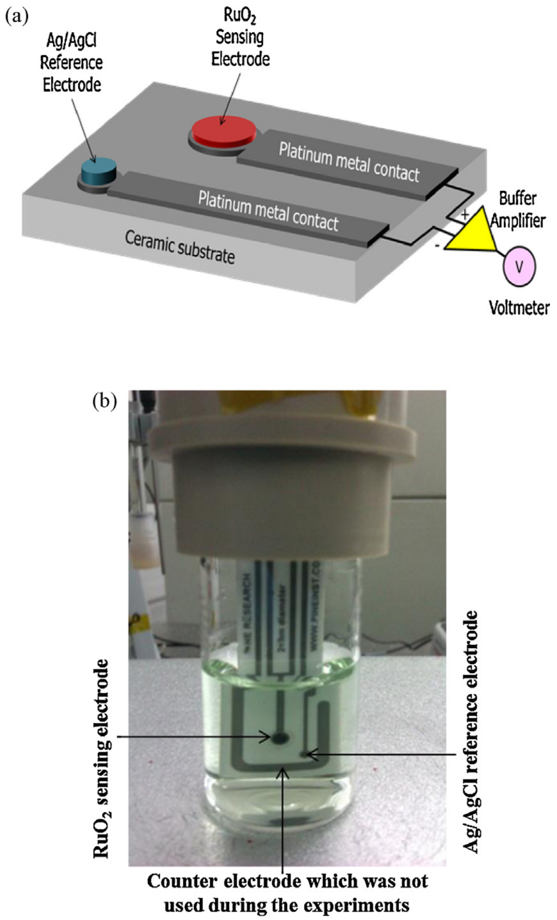

Fig. 1. (a) Structure of the pH sensor. (b) Microphotograph of fabricated pH sensor.

Experimental results demonstrate excellent features of the pH sensor, including high sensitivity, fast time response, high resolution, reversibility and repeatability.

2. Sensor fabrication and measurements

2.1. Sensor fabrication

The generic structure of the developed pH sensor is shown in Fig. 1(a) [11]. It consists of an alumina substrate on which two platinum contacts are first deposited. To realise the sensing electrode, a sub-micron RuO_2 thin film is R.F. sputtered on top of one of the platinum contact. On the other hand, the Ag/AgCl reference electrode is realised by printing a thick Ag film on the other platinum contact followed by the formation of an AgCl film through electroplating. In the experiments, the pH sensors were made by using an off-the-shelf ceramic patterned electrode cells of dimensions 15 mm × 61 mm × 0.67 mm developed by Pine Research Instrumentation (http://www.pineinst.com), comprising a patterned platinum sensing contact and an electroplated Ag/AgCl reference electrode of sensing diameters 2 mm and 1 mm, respectively, as shown in Fig. 1(b). Note that the 2 mm diameter for the sensing electrode exceeds the minimum required diameter for stable operation [12]. We used an R.F. magnetron sputtering system (in conjunction with shadow masking) to deposit RuO_2 thin films onto the platinum sensing electrode area of the electrode cell. A 99.95% pure, 4-inch diameter RuO_2 sputtering target was used to sputter 50 nm, 175 nm and 300 nm RuO_2 thin-films in argon and oxygen plasma. The deposition process parameters that were used to fabricate the RuO_2 thin films are listed in Table 1. Note that the deposited RuO_2 thin films were not sintered.

Table 1
Sputtering process parameters for RuO_2 sensing film deposition.

Target	RuO_2 (99.95% pure)
Process gas	90% Ar + 10% O_2
Substrate temperature	Room temperature
RF power	100 W
Process pressure	1 mTorr
Deposition rate:	0.35 Å/s

2.2. pH measurement

An Agilent 34410A high performance digital multimeter was used to record the potential difference between the electrodes of the pH sensor in real-time. A unity-gain buffer amplifier was developed and used for impedance matching and signal loss minimisation. The electrochemical behaviour of the sensor was investigated through potentiometric measurements. The potential difference between the RuO_2 sensing electrode and the Ag/AgCl reference electrode was recorded with 20 s intervals for test solutions of pH 4, pH 7 and pH 10 at 22 °C (temperature of our cleanroom), which were purchased from Rowe Scientific, Australia and used to characterise the sensor. The test solutions were continuously stirred using a magnetic stirrer for quicker equilibrium of ion concentrations around the sensing electrodes [4]. During the experiments, the measured pH values of the test solutions were compared with the pH values measured by an Oakton pH metre (pH 700 benchtop metre), and the sensor was cleaned after each pH measurement using DI water rinse followed by N_2 drying.

3. Results and discussion

3.1. pH sensing mechanism

Fog and Buck proposed five possible interpretations for the pH response mechanism of metal oxides, with the most accepted theory being oxygen intercalation [6,11–13]. The oxygen intercalation mechanism is represented by the following equilibrium reaction [8,13,14]:

$$MO_x + 2\delta H^+ + 2\delta e^- \leftrightarrow MO_{x\_\delta} + \delta H_2O \quad (1)$$

where δ is the intercalation of interstitial oxygen, MO_x is a higher metal oxide and MO_{x_δ} is a lower metal oxide.

The Pourbaix Atlas has been used for explaining the mechanism governing redox equilibrium between two insoluble ruthenium oxides, which is governed by the following reaction.

$$RuO_2 + 2H_2O + H^+ + e^- \leftrightarrow H_2O + Ru(OH)_3 \quad (2)$$

The Nernst's mathematical equation predicting the potential between the sensing and reference electrodes versus the pH value is given by:

$$E = E^0 - 2.303\frac{RT}{F}\ \mathrm{pH} = E^0 - 0.05916\ \mathrm{pH} \quad (3)$$

where E^0 is the reference electrode potential, R is the gas constant, T is absolute temperature and F is Faraday's constant. The entire term 2.303 RT/F is called the Nernst slope. The Nernst slope is 59.16 mV/pH at 25 °C.

3.2. Sensor performance

3.2.1. Sensitivity

The sensitivity of pH sensor was validated by immersing the sensor in pH buffer solution of pH 4, pH 7 and pH 10 at 22 °C. Each