Materials Letters 75 (2012) 165–168

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Influence of thickness of sub-micron Cu_2O-doped RuO_2 electrode on sensing performance of planar electrochemical pH sensors

Serge Zhuiykov [a,*], Eugene Kats [a], Kourosh Kalantar-zadeh [b], Michael Breedon [c,d], Norio Miura [c]

[a] CSIRO, Materials Science and Engineering Division, 37 Graham Road, Highett, VIC, 3190, Australia
[b] RMIT University, School of Electrical and Computer Engineering, Melbourne, VIC, 3001, Australia
[c] KASTEC, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan
[d] Japan Society for the Promotion of Science, Tokyo 102-8471, Japan

ARTICLE INFO

Article history:
Received 19 January 2012
Accepted 24 January 2012
Available online 31 January 2012

Keywords:
Cu_2O
RuO_2 sensing electrode
pH sensors

ABSTRACT

Influence of thickness of sensing electrodes (SEs) based on screen-printed sub-micron Cu_2O-doped RuO_2 films on characteristics of the planar pH sensors has been investigated. It was determined that as thickness of Cu_2O-doped RuO_2-SE increased from ~2.0 μm to ~5.0 μm, variations in the sensor's pH sensitivity were negligible. However, the sensor's response time improved from ~80–120 s for SE with thickness of 2.0 μm to ~25 s for SE with thickness of 5.0 μm. The enhancement of dynamic characteristics is potentially related to the establishment of the improved-structured “thick” SE, as more advanced crystallisation is achieved as thickness increased. Moreover, morphology of the “thick” SE revealed both the presence of “inner” active surfaces within SE and the developed open porosity of SE.

1. Introduction

Comprehensive *on-line* monitoring of water quality on the high spatial resolution is inseparably connected with simultaneous development of a new generation of wireless sensor networks and accurate, inexpensive, robust and miniaturised sensors based on thin- or thick-film semiconductor SE [1–7]. Since both *thin*- and *thick*-film technologies are equally viable choices for the fabrication of planar pH sensors based on doped oxide-SEs, it is necessary to establish how thickness of the SE influences the sensing performance of these sensors. To the best of our knowledge, no study has been dedicated so far to such analysis with specific relevance to the water quality sensors. Few investigations, devoted to the better understanding of the influence the structure and thickness of SE, were conducted for nanostructured gas sensors [8–12]. However, these studies have only concluded that the influence of SE thickness is very complicated and depends on the nature of the target gas [11], the required operational temperature [12] and the grains size and their orientations [10,12].

Essentially, planar solid-state water quality sensors can be represented as a “sandwich” structure, with one or several SEs deposited on the surface of the sensor's substrate. Advances in nanotechnologies provided nano-dimensional particles of high purity and extremely high surface-to-volume ratios, coupled with affordable fabrication processes offering good control of particle size, morphology and porosity. Considering such advances, the overall sensors' performance can be improved by intelligent selection not only the suitable doped SE materials [13], but also by optimization of their microstructures and thickness. Therefore, this research represents the first study of the influence of thickness the sub-micron Cu_2O-doped RuO_2-SE on the sensing performance of planar electrochemical pH sensors.

2. Experimental

The fabrication procedure for the planar ceramic pH sensor featuring 4 screen-printed SEs with different thicknesses, involved screen-printing 2-, 4-, 6- and 8-layer SEs onto the same alumina sensor substrate. 20 mol% Cu_2O-doped RuO_2-SEs were fabricated from high-purity analytical grade RuO_2 and Cu_2O nano-particles, as described elsewhere [13]. In brief, 4 Pt current conductors with thicknesses of ~5 μm were applied onto an alumina substrate and sintered at 1000 °C for 1 h in air prior to the deposition of 20 mol% Cu_2O-doped RuO_2-SEs. SE paste used to print the film-SEs was obtained by mixing Cu_2O and RuO_2 nano-powders with an organic α-terpineol ($C_{10}H_{18}O$, 99.9%) as a binder [1]. Subsequently 4 SEs were simultaneously sintered at 800 °C.

The thickness of the Cu_2O-doped RuO_2-SEs was determined via direct observation of the cross-section of the SE/substrate interfaces by using a HELIOS-Nanolab-600 (Netherlands) field emission beam scanning electron microscope (FIB-SEM) with a Ga beam. The same FIB-SEM was also used to characterise the surface morphology of the prepared SE films. X-ray diffraction (XRD) patterns for thin- and thick-SEs were obtained on Rigaku, RINT 2100VLR/PC apparatus using CuKα radiation in flat plane θ/2θ geometry between 20° and 80°.

Sensing performance of the devices attached with 20 mol% Cu_2O-doped RuO_2-SEs of the different thicknesses was investigated on the conventional water-flow apparatus. An external Ag/AgCl, Cl^- reference

---

* Corresponding author. Tel.: +61 39252 6236.
E-mail address: serge.zhuiykov@csiro.au (S. Zhuiykov).

0167-577X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2012.01.107

electrode was employed for potentiometric measurements. The temperature was monitored using a type-K thermocouple mounted adjacent to the sensor, with the pH controlled by titration of standard sodium hydroxide and hydrochloric acid solutions. The sensor's sensitivity and response time for 20 mol% Cu_2O-doped RuO_2 film-SEs with different thicknesses were evaluated by means of potentiometer measurements obtained from the electrometer. Time constants of transient processes were determined on the 0.9 level of a steady state value of measured potential difference.

3. Results and discussion

A graphical illustration of the cross-sectional view of the developed 20 mol% Cu_2O-doped RuO_2-SE structure depicting the tortuous paths that the charge carriers must take to the Pt current conductor is shown in Fig. 1. One can see that the surface SE layer is made of complex oxide crystallites separated by highly defective regions. Thus, three types of interfaces should be considered: (I) the oxide SE/solution macro-boundaries (*outer surface*); (II) the oxide SE/solution micro-boundaries due to penetration of the liquid into pores and inter-grain regions (*inner surface*); (III) the oxide SE layer/support Pt layer interface. As far as the sensor's performance is concerned, the first two interfaces are of the greatest importance.

Fig. 2 elaborates how FIB cuts were made on thin- and thick-film 20 mol% Cu_2O-doped RuO_2-SEs as well as the measured thickness of SEs. It can also be clearly observed from the angled SEM images, that the thin- (Fig. 2(a)) and thick- (Fig. 2(b)) SEs exhibited different morphologies. One can see that as the film became thicker, the pore size also increases, confirming that the thicker the film-SE, the more porous it is [12]. Apparently, the thin-film-SE is more densely packed due to its smaller grain size. To confirm this assumption, measurements of the several grain sizes of film-SEs were conducted by using FIB cut in the structure of SE. Analysis of these measurements revealed that the thickness of the thin-film-SE was less than 2.0 μm with the average grain size of approximately 600–800 nm (Fig. 2(c)) and the thickness of the thick-film-SE varied from 4.0 to 5.0 μm with the average of grain size of about 1.5–2.0 μm (Fig. 2(d)). Unfortunately, the focused Ga beam of the FIB smoothed the interface during the etching. As a result, the roughness of the developed interfaces cannot be directly observed. The etched regions of

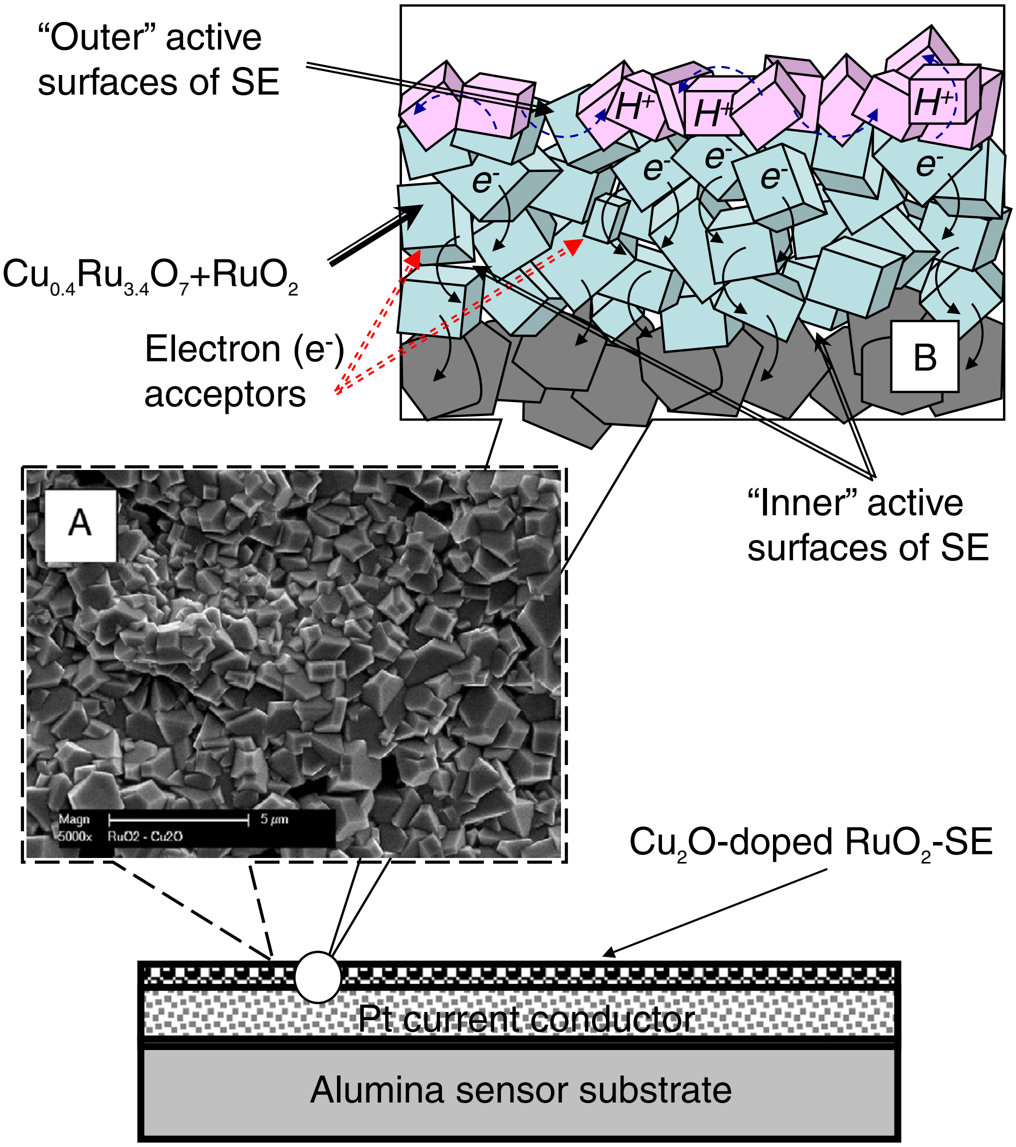

Fig. 1. A cross-sectional view of the sensor substrate featuring a 20 mol% Cu_2O-doped RuO_2-SE showing a SEM image of the surface of SE (A) and tortuous paths of charge carries to the Pt current conductor (B).