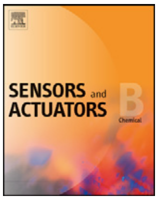
Sensors and Actuators B 137 (2009) 762–767

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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



Ruthenium dioxide quartz crystal nano-balance

Konstantinas Leinartas, Povilas Miečinskas, Eimutis Juzeliūnas*

Institute of Chemistry, A. Goštauto 9, 01108 Vilnius, Lithuania

ARTICLE INFO

Article history:
Received 23 October 2008
Received in revised form
21 November 2008
Accepted 3 December 2008
Available online 11 December 2008

Keywords:
QCM
QCN
Ruthenium dioxide
Mass sensor
Water adsorption
Copper deposition

ABSTRACT

A new type of quartz crystal nano-balance (QCN) has been designed using ruthenium oxide (RuO_2) electrodes as substitutes for the metallic ones, which are generally used to prepare QCN sensors. The conductive RuO_2 electrodes were deposited on quartz discs using reactive magnetron sputtering. XPS measurements showed the ratio of atomic concentrations [Ru]/[O] close to 1:2. XRD indicated crystalline structure of the deposits and AFM showed highly developed surface with pits and other features of various sizes. The oxide-based resonator operated stable in both gaseous and liquid environments as demonstrated by the prolonged experiments of water adsorption–absorption in humid air and electrochemical copper deposition–dissolution in acid solution. The sensor opens new opportunities to study thin films of RuO_2. One of the advantages of the sensor is possibility to avoid the galvanic effects, which may occur when using the conventional QCN with metallic electrodes.

1. Introduction

Quartz crystal micro- or nanogravimetry (QCM, QCN) is widely used for various scientific and technical applications and its principles were well surveyed [1–4]. The origin of microgravimetry goes as far back as the middle of the 20th century, when *Sauerbrey* published in 1959 the results of investigation on how oscillation frequency of quartz resonator depends on the foreign mass added to or removed from the oscillator surface [5]. Relatively soon after the invention, QCM attracted attention of corrosion researchers. Littler has first used the QCM for corrosion studies and patented the approach in 1966 [6].

It was a belief for a rather long time that Sauerbrey's ratio is not applicable for solutions, as it assumes that the oscillator surface does not undergo any shear deformations during the oscillation, which is well true for thin rigid films, e.g. metal coatings. In 1980, studies appeared, which showed that the QCM is applicable also to liquids [7,8]. Some years later, Bruckenstein with co-workers used QCM for electroanalytical purposes *in situ*, in particular to weigh monolayer amounts of materials deposited on electrodes [9,10]. Kanazawa et al. derived the ratio for the oscillator frequency shift exerted by a liquid [11], which was found to be in good agreement with the sucrose concentration reported by Nomura [8]. Soon after these works, more papers appeared in QCM application in solutions electrochemistry [12–17] and later on the technique became routinely used in electrochemistry. The advantages of the method include high sensitivity, non-invasive measurements in-situ and in real time and possibility to simultaneously perform other measurements (e.g. spectroscopy). At the same time, the method has a serious drawback: the materials to be studied by QCN are limited to those electroplated, evaporated or sputtered. Some expanding of the field suggested application of glued foil electrodes [18,19].

The QCM technique employs the quartz crystal oscillators with metallic electrodes, typically inert ones such as gold and platinum. An oxide electrode has also been applied to study properties of polypyrrole [20]. Indium tin oxide (ITO) was heat-treated at 500 °C and had resonant resistance of 30 Ω. The ITO based QCM was used in conjunction with UV–visible spectroscopy and voltammetry to study the redox processes in polypyrrole films.

In this paper we report a new type of quartz oscillator, which is free from the metallic coatings. Instead of metal, a conductive ruthenium dioxide (RuO_2) was used as an electrode material to induce oscillations in quartz crystal. To our best knowledge, this is the first attempt to develop the RuO_2 QCM.

Two main types of ruthenium dioxide show great promise in various technical applications: the hydrous oxide $RuO_2 \times xH_2O$, which has a mixed electron–proton conductivity [21,22], and the anhydrous one, which exhibits a metal-like conductivity [23]. Apart from a high electric conductivity, both types exhibit also a high catalytic activity, super-capacitance properties, chemical inertness and thermal stability. The properties of anhydrous oxide depend on formation conditions, for instance, the texture and resistivity of RuO_2 deposited by magnetron sputtering was shown to be dependent on deposition power, oxygen pressure and O_2/Ar ratio,

---

* Corresponding author.
E-mail address: ejuzel@ktl.mii.lt (E. Juzeliūnas).

0925-4005/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2008.12.003

temperature and substrate properties [24,25]. Studies were performed with perfect (epitaxial) anhydrous RuO_2 films grown in the form of lattice-multilayers on various substrates [26,27].

RuO_2 is attractive for microelectronics industry to fabricate precise thin-films resistors, interconnections, gate electrodes, diffusion barriers, electrochromic materials, hydrocarbon sensors, etc. [28,29]. In electrochemical industry, RuO_2 based electrodes have been used for many years in chlorine and alkali production due to possibility to run hydrogen and chlorine evolution reactions at low overpotentials [30–32]. Electrochemistry of Ru and RuO_2 electrodes as well as the mixtures with other oxides, e.g. IrO_2, TiO_2, Co_3O_4, SnO_2 was widely studied [33–44]. Catalytic activity of RuO_2 in electro-oxidation of alcohols, hydrogen, CO and ammonia makes it applicable in fuel cells [45–52]. The high metallic electronic conductivity of RuO_2 along with its excellent chemical and thermal stability makes this material promising as a durable nanowire in the presence of water and oxygen [53]. Another important property of the ruthenium oxide is extremely large pseudo-capacitances. Ruthenium oxide, has been shown to be probably the best electrode material in terms of a high specific capacitance, a wide potential window and a long shelf and cycle life [54,55]. Especially the amorphous hydrous RuO_2 exhibited a high specific capacitance (over $800\,\mathrm{F\,g^{-1}}$) [56–58]. Amorphous anhydrous RuO_2 films were deposited by the spray pyrolysis method with a rather high specific capacitance ($551\,\mathrm{F\,g^{-1}}$) [59].

We developed the RuO_2 QCN with the aim to study nano-scale mass effects, which are of interest in the various RuO_2 research fields mentioned above. As first applications of the QCN, we report here the water uptake by the oxide both in air and solutions as well as copper deposition–dissolution using cyclic polarization mode.

2. Experimental

Thin layers of RuO_2 ($d \approx 0.2$–$0.25\,\mu\mathrm{m}$) were deposited by reactive magnetron sputtering on quartz discs (AT cut) manufactured by "KVG Quartz Crystal Technology GmbH" (Germany). The diameter of discs was 15 mm. Prior to the deposition procedure the quartz surfaces were cleaned ultrasonically in pure acetone (99.999). The target was prepared from a pure Ru powder by pressing it into the disc specimen 25–30 mm in diameter. The quartz substrates were positioned at a distance of 30–40 mm above the target. The MS chamber was evacuated to the pressure of 1.33×10^{-4} Pa. The plasma discharge was executed in atmosphere of Ar–O_2 mixture (4:1) at a total pressure of 5–10 Pa and temperature $T \approx 300\,^{\circ}\mathrm{C}$. According to calibration data, the oxide deposition rate for discharge current density of $j = 3.1\,\mathrm{mA/cm^2}$ was about $1 \times 10^{-10}\,\mathrm{m\,s^{-1}}$.

The elemental composition of the deposits was analyzed by X-ray photoelectron spectroscopy (XPS). The spectra were recorded by an "ESCALAB MK" spectrometer (UK) using X-ray radiation of Mg K_α (1253.6 eV, pass energy −20 eV). The samples were etched in the preparation chamber by ionized Ar at the vacuum of 5×10^{-4} Pa. An accelerating voltage of 15 kV and a beam current of $20\,\mu\mathrm{A/cm^2}$ corresponded to the surface etching rate of *ca.* 2 nm/min.

X-ray diffraction (XRD) measurements were carried out by a D8 Advance diffractometer from "Bruker AXS" (Germany) with Cu K_α radiation selected by a secondary graphite monochromator. The scan mode with the steps of $2\theta = 0.04^\circ$ and a sampling time of 3 s/step in the range $5^\circ \le 2\theta \le 70^\circ$ was used.

The surface micromorphology of RuO_2 was studied by a scanning atomic force microscope (AFM) "TopoMetrix Explorer SPM" (USA). The images were obtained with Si_3N_4 tip in the contact mode at ambient temperature.

The quartz discs for QCN had the fundamental frequency $f_0 = 5$ MHz, which proportional coefficient according to Sauerbrey's equation [5] between the frequency and the mass change was $C \approx 18\,\mathrm{ng\,Hz^{-1}\,cm^{-2}}$. The disc with RuO_2 was mounted in a special window of a Teflon cell, with one side exposed to the cell compartment. Frequency generation and the stability of the RuO_2 resonator was checked exposing it to air or to the following solution: 0.08 M $CuSO_4$ + 0.05 M H_2SO_4. The solutions were prepared from analytical grade purity reagents and triply distilled water.

The measurements in atmosphere were performed using a Teflon hermetic cell. The cell compartment (40 mm × 50 mm × 40 mm) was supplied with a 0.9N NaCl solution (10 mm layer). The solution was saturated by Ar gas applying a slow gas flow rate of $\sim 0.3\,\mathrm{cm^3/min}$ which maintained the relative humidity in the cell close to a saturated one. Measurements were conducted at ambient temperature, its change during the 6 h experiment did not exceed $\pm 0.5\,^{\circ}\mathrm{C}$.

3. Results and discussion

Two operating temperatures $T = 100$ and $300\,^{\circ}\mathrm{C}$ were examined for ruthenium dioxide deposition by magnetron sputtering. Higher temperatures were not applied to avoid impact on the properties of quartz substrate. For both temperatures, the electrical resistance of the deposited films, measured by the four-probe method, was $R < 70\,\mu\Omega\,\mathrm{cm}$. However, the oxide film sputtered at $300\,^{\circ}\mathrm{C}$ had better adhesion to quartz surface. The experiments, therefore, provided below were carried out using the specimens prepared at $300\,^{\circ}\mathrm{C}$.

XPS spectra of the deposits and the elemental content are given in Fig. 1 and Table 1. It should be noted that the binding energies (E_b) for different oxidation states of ruthenium are very similar, e.g. for $Ru3d_5$: $E_b = 282.0$ eV for RuO_2, $E_b = 282.3$ for RuO_3 and $E_b = 283.0$ eV for RuO_4 [60,61]. Thus, strict identification of the oxides from XPS peaks is rather complicate. Nevertheless, the ratio of atomic concentrations [Ru]/[O] was found to be close to 1:2, which indicates RuO_2 (Table 1). The data also show that the top of the oxide structure is enriched by oxygen (Ru—16% vs. O—84%), which points to higher oxidation states of ruthenium (e.g. RuO_3 and RuO_4).

X-ray diffraction data indicated RuO_2 to be a predominant component in the oxide coating (Fig. 2). The data confirmed a crystalline structure of the deposits with tetragonal crystals. The lattice parameters were found $a = b = 0.4499$ nm, $c = 0.31071$ nm [62]. The crystals had prevailing orientation $\langle 1\,0\,0 \rangle$ and the grain size according to Sherrer's equation was $D > 250$ nm [63].

The operational stability of the RuO_2 sensor in gaseous environment was examined by a long term experiment (6 h) of water uptake in air (Fig. 3). The mass gain dynamics was registered by exposing the ruthenium oxide to air, whose humidity was close to 100%. A rapid frequency decrease (mass growth) is observed during the first hour of exposure, while later on, the frequency decrease is getting slower approaching some limit. The mass gain is due most likely by two processes: water adsorption and absorption. Adsorption means water bounding to the oxide surface and further attachment at water/air interface. The absorption process is due to water entering the oxide film through pores or other features, e.g. due to capillary

Table 1
Content of elements in sputtered ruthenium oxide.

Depth (nm)	Element	Atomic percentage (%)
0	Ru	16.04.0
	O	84.0
1.0	Ru	27.0
	O	73.0
3.0	Ru	33.7
	O	66.3
6.0	Ru	35.4
	O	64.6