Long-term Monitor of Seawater by using TiO₂:Ru Sensing Electrode for Hard Clam Cultivation

Jung-Chuan Chou, and Cheng-Wei Chen

Abstract—The hard clam (meretrix lusoria) cultivated industry has been developed vigorously for recent years in Taiwan, and seawater quality determines the cultivated environment. The pH concentration variation affects survival rate of meretrix lusoria immediately. In order to monitor seawater quality, solid-state sensing electrode of ruthenium-doped titanium dioxide (TiO2:Ru) is developed to measure hydrogen ion concentration in different cultivated solutions. Because the TiO2:Ru sensing electrode has high chemical stability and superior sensing characteristics, thus it is applied as a pH sensor. Response voltages of TiO2:Ru sensing electrode are readout by instrument amplifier in different sample solutions. Mean sensitivity and linearity of TiO2:Ru sensing electrode are 55.20 mV/pH and 0.999 from pH1 to pH13, respectively. We expect that the TiO₂:Ru sensing electrode can be applied to real environment measurement, therefore we collect two sample solutions by different meretrix lusoria cultivated ponds in the Yunlin, Taiwan. The two sample solutions are both measured for 200 seconds after calibration of standard pH buffer solutions (pH7, pH8 and pH 9). Mean response voltages of sample 1 and sample 2 are -178.758 mV (Standard deviation=0.427 mV) and -180.206 mV (Standard deviation =0.399 mV), respectively. Response voltages of the two sample solutions are between pH 8 and pH 9 which conform to weak alkali range and suitable meretrix lusoria growth. For long-term monitoring, drift of cultivated solutions (sample 1 and sample 2) are 1.16 mV/hour and 1.03 mV/hour, respectively.

Keywords—Co-sputtering system, Hard clam (meretrix lusoria), Ruthenium-doped titanium dioxide, Solid-state sensing electrode.

I. INTRODUCTION

HARD calm (meretrix lusoria) cultivated industry is developed recently in Taiwan, especially focuses on southwest seacoast there. Massive die-offs of the economical product impact directly incomes of fishermen. The salinities of pond water in the former are normally maintained within the usual range (25%–33%) by continually exchanging pond water with seawater, while those in the latter range between 15% and 20% by the addition of groundwater with salinities of 13%–17% [1]. Important factors of seawater quality in

Jung-Chuan Chou is with the Graduate School of Electronic Engineering, National Yunlin University of Science and Technology, 123, Sec.3, University Rd. Douliou, Yunlin, Taiwan (R.O.C.) 64002. (corresponding author to provide phone: 8865-534-2601 ext. 2101; fax: 8865-532-1719; e-mail: choujc@yuntech.edu.tw).

Cheng-Wei Chen is with the Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology, 123, Sec.3, University Rd. Douliou, Yunlin, Taiwan (R.O.C.) 64002. (e-mail: g9610803@ yuntech.edu.tw).

cultivated ponds consist of pH concentration, temperature, dissolved oxygen and transparency, etc. [2, 3].

pH concentration varies with reaction of submerged organism as photosynthesis and respiration (6CO₂+6H₂O \rightarrow $C_6H_{12}O_6+6O_2$), fermentation ($C_6H_{12}O_6+3CO_2 \rightarrow 3CH_4+6CO_2$), nitrification $(NH_4^++2O_2 \rightarrow NO_3^-+H_2O+2H^+)$, oxysulfide $(HS+2O_2 \rightarrow SO_4^{2-}+H^+, \text{ sulfide reduction } (C_6H_{12}O_6+3SO_4^{2-})$ $+3H^{+} \rightarrow 6CO_{2}+3HS+6H_{2}O$) and so on. The best growth environment for hard clam is shown that the pH concentration between pH 7.5 and pH 8.5, temperature is between 25 °C and 32 °C, salinity is from 18 % to 25 %, water depth is about 45 cm approximately and sandy content is between 60 % and 80 %. Furthermore, massive die-offs of hard calm arise from seasonal variation and pouring rain [4]. However, primary factors of affection in cultivated quality and mass production are still unknown, thus cultivated technique is dependant on experience of fishermen themselves [5]. We expect to provide a high sensitivity, linearity, solid-state sensing electrode and cost down than commercial pH meter which applied to monitor effectively seawater quality variation of cultivated ponds for long-term measurement.

Because of titanium dioxide (TiO₂) has superior parameters such as relatively high photocatalytic activity, biological and chemical stability, low cost, non-toxic nature, long-term stability, high index of refraction, high dielectric constant and high hardness, thus it was used for many application fields. [6-11]. However, intrinsic titanium dioxide has larger sheet resistance and less conductivity; therefore, the carrier mobility is less than other metal oxides such as indium tin oxide (ITO), tin dioxide (SnO₂) and so on. In this investigation, we present a metallic modification for titanium dioxide (TiO₂) which decreases resistivity of TiO₂ sensing film, and increases carrier mobility for solid-state sensing electrode. Therefore, the ruthenium (Ru) ions are utilized to dope into TiO₂ sensing film by co-sputtering system.

II. EXPERIMENTAL

A. Chemicals, Reagents and Materials

Silicon wafer is used for substrate of sensing film which is p-type, resistivity for 15-25 Ω -cm, (100)-oriented and supported by National Nano Device Laboratories (NDL). TiO₂ target and ruthenium target were purchased by Ultimate

Materials Technology Co., Ltd in Taiwan, and both formation from a 2-in. diameter, 1/4 in. thickness and 99.99% purity. pH standard solutions from pH1 to pH13 were purchased by Riedel-deHaen, Sigma-Aldrich Co., Ltd in USA. Hard clam cultivated solutions were collected in Taishi, Yunlin, Taiwan.

B. Fabrication of the TiO₂:Ru sensing film

In this study, co-sputtering system is used to fabricate the ruthenium-doped titanium dioxide (TiO2:Ru) sensing film which is deposited on p-type silicon substrate. The co-sputtering system consists of a radio frequency (R.F.) power generator and a direct current (DC) power supply, which sputters simultaneously. Radio frequency (R.F.) power generator and direct current (DC) power supply are set at 100 watt and 30 watt, respectively. Working pressure is around 30 mtorr for 1 hour. Argon and oxygen gases are introduced into reactive chamber which are 40 sccm and 2 sccm, respectively. Metal contact is silver paste which connects between sensing film surface and gate of MOSFET (CD4007UB). Sensing area size of TiO₂:Ru sensing electrode is defined and packaged by epoxy resin which can avoid current leakage. Fig. 1 shows that separative extended gate field effect transistor (SEGFET) is formed as TiO₂:Ru-based pH sensor. MOSFET (CD4007UB) is kept to work in linear region. Drain-Source voltage is set at 0.2V.

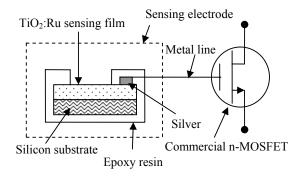


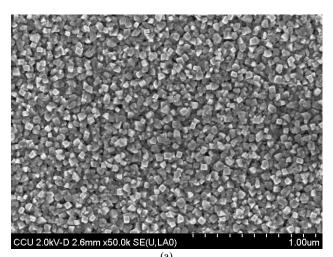
Fig. 1 Structure of TiO₂:Ru-based separative extended gate field effect transistor (SEGFET) is measured for I-V measurements

III. RESULTS AND DISCUSSION

A. Surface Morphology of the Ruthenium-Doped Titanium Dioxide

Surface performance of sensing film is one of the important factors for sensing characteristics. Therefore, we used field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) to verify surface morphology and roughness of TiO₂:Ru sensing film, respectively. The TiO₂:Ru sensing film is treated for thermal annealing at 600°C for 1 hour in the atmosphere by conventional thermal annealing (CTA) before surface observation which makes crystalline arrangements. Fig. 2(a) shows the surface morphology of TiO₂:Ru for optimal deposition parameters. It illustrates that the surface crystallization appears cubic lattice, and its scale size is shown from 30nm to 60nm approximately. Surface of

the TiO_2 :Ru sensing film has high specific surface area that increases H^+ ions absorption rate for unit area. Furthermore, TiO_2 :Ru sensing film has high hydrophilic characteristic and porosity that suits to apply as electrochemical sensors and increases easily sensing signal transduction. The cubic crystal structure provides more ion surface absorptions for unit area. Fig. 2(b) shows the surface roughness image of three dimension that the mean roughness of TiO_2 :Ru sensing film is 7.2nm. Because surface roughness has superior uniformity which can reduce point discharges at solution/sensing film interface, and increase hydrogen ions absorption.



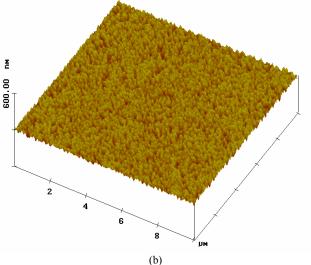


Fig. 2 (a) Surface morphology of TiO₂:Ru film is measured by FE-SEM; (b) Surface roughness of TiO₂:Ru film is measured by AFM

B. pH Sensing Characteristics of the TiO₂:Ru-based Electrode

Sensitivity is one of important parameters for SEGFET sensor. Sensitivity is defined that the sensing film surface induces relative surface potential between solution and sensing membrane interface. I_D - V_{ref} curves of SEGFET sensor are measured by I-V measurement system (Keithley 236 Current

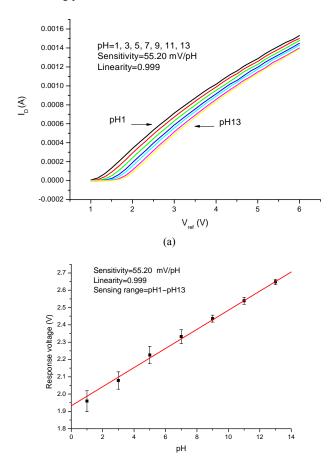
Measure Unit). Measurement data are analyzed by Origin Pro. 7.0 software, and then we can obtain sensitivity ($\Box mV/\Box pH$) of SEGFET sensor.

pH sensing performance for TiO₂:Ru-based SEGFET structure is defined. SEGFET is operated in non-saturation (linear) region which is as follows [12-15]:

$$I_{D} = K_{n}[2(V_{ref} - \Delta V_{TEG})V_{DS} - V_{DS}^{2}]$$
 (1)

where I_D is the drain current, K_n is the conduction parameter for n-channel enhancement mode, V_{Ref} is the scanning reference electrode voltage, and ΔV_{TEG} is the threshold voltage difference of SEGFET in different pH solutions, and V_{DS} is the drain-source voltage of SEGFET.

I-V curves and linear curve for TiO₂:Ru SEGFET-based sensor are shown in Fig. 3(a) and Fig. 3(b), respectively. Sensitivity and linearity of the TiO₂:Ru SEGFET-based sensor are calculated with Origin Pro. 7.0 in constant current (200mA) from pH1 to pH13 which are 55.20 mV/pH (S.D. =2.81 mV/pH) and 0.999, respectively. Because TiO₂:Ru-based SEGFET sensor has superior sensing characteristics and stability, thus it is utilized to apply as solid-state pH sensor for monitoring pH values of hard calm cultivated solutions.



(b)
Fig. 3 (a) I-V curves of TiO₂:Ru-based SEGFET are measured from pH1 to pH13; (b) Sensitivity and linearity of TiO₂:Ru-based SEGFET are measured from pH1 to pH13

Interface between TiO₂:Ru-based solid-state sensing electrode and sample liquid has a reactive potentials, and its sensing mechanism is as follows [12-15]:

$$\phi^{s} - \phi^{l} = (\frac{1}{F})(\mu_{H^{+}}^{l} + \mu_{e^{-}}^{s} + \frac{\mu_{O}^{s}}{2} - \frac{\mu_{H_{2}O}^{l}}{2}) = \text{constant} + \frac{RT}{F} \ln a_{H^{+}}^{l}$$

$$-\frac{\mathrm{RT}}{\mathrm{F}} \ln \mathrm{a}_0^{\mathrm{s}} \tag{2}$$

where the $\mu_e^{s_-}$ denotes chemical potentials (the chemical potentials of pure phases are constants), s and l denote solid and liquid, respectively, $\phi^s - \phi^l$ denotes the interface potential, a_H^l , and a_0^s denote the activity of hydrogen ions in the liquid phase and activity of oxygen in the solid phase, respectively. According to Eq. (2), it expresses that activity of sample liquid determines the difference of potential response between sample liquid and solid-state interface. The $H^+ - O^{2-} - H^+$ bonding is one of determinable methods which can affect sensitivity directly.

Response time of TiO_2 :Ru-based solid-state sensing electrode in pH standard buffer solution from pH1 to pH13 are all shorter then 1 second. However, response time of TiO_2 :Ru-based solid-state sensing electrode in hard clam cultivated solutions has larger response time where are shown in Fig. 4.

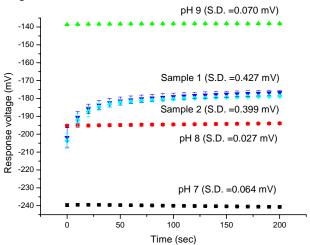


Fig. 4 Short-term responses for pH measurements of sample liquids are between 0 and 200 seconds

In order to provide for a based reference level and potential calibration, the TiO₂:Ru-based sensing electrode is immersed in pH7, pH8 and pH9 for pH standard solutions which are measured for 200 seconds. Their mean response voltages and standard deviations are -240.37 mV (S.D. =0.064 mV), -194.566 mV (S.D. =0.027 mV) and -138.195 mV (S.D. =0.070 mV), respectively. And then TiO₂:Ru-based sensing electrode is measured in hard clam cultivated solutions for sample 1 and sample 2 for 200 seconds, respectively. Because of hard clam cultivated solution is collected from cultivated ponds of Taishi (Yunlin country in Taiwan), thus it has more other interference ions to affect hydrogen ionic exchange such as Na⁺, Mg²⁺, K⁺

and so on. Therefore, Short-term responses (larger than 95%) of hard clam cultivated solutions (sample 1 and sample 2) are less than 40 seconds. Their mean response voltages and standard deviations between 41 seconds and 200 seconds are -178.758 mV (S.D. =0.427 mV) and -180.206 mV (S.D. =0.399 mV), respectively. Measurement temperature is maintained at 25±0.1°C.

Solid-state sensing electrode has a non-ideal effect which is long-term drift effect, thus we further investigated about time-dependent on response voltages. Drift rate is defined from the International Union of Pure and Applied Chemistry (IUPAC) which is the slow non-random change with time in the electromotive force (emf) of an ion-selective electrode cell assembly maintained in a solution of constant composition and temperature. The slope of the emf versus time line is called drift.

Literatures reported the measured data were fitted to multiple time-constant step-response curves that are as follows [12-15]:

$$O(t) = S \Delta p H \left[1 - \sum_{i=1}^{j} \varepsilon_i \exp\left(-\frac{t}{\tau_i}\right)\right] + \frac{\Delta O}{\Delta t} t \quad \text{for } t > 0$$
 (3)

where O(t) denotes the offset and temperature-corrected form the sensor signal, S is the total pH-sensitivity, ΔpH is the amplitude of the pH-step, ϵ_i and τ_i are the normalized amplitude and time constant of the corresponding exponential term i, respectively, and $\Delta O/\Delta t$ is the drift of sensor. $\Delta O/\Delta t$ was obtained from the temperature-corrected sensor signal by a linear approximation of the time interval between 5 hours and 12 hours after the pH-step. Long-term drift measurements of pH standard buffer solutions from pH7 to pH9 and cultivated solutions for TiO₂:Ru-based pH sensor are exhibited in Fig. 5.

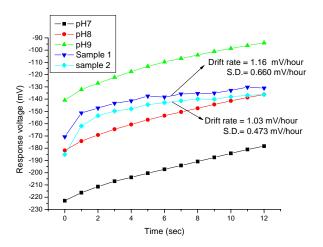


Fig. 5 Long-term responses for pH measurements of sample liquids are between 0 and 12 hours

According to the experimental results, drift rates and standard deviation from 5 hours to 12 hours for cultivated solutions (sample 1 and sample 2) are 1.16 mV/hour (S.D. =0.660 mV/hour) and 1.03 mV/hour (S.D. =0.473 mV/hour), respectively, where are listed in Table I. To compare with references [15-17], amorphous material has larger drift rate

generally because it provides more chance to absorb OH - ions, and increases potential response. Metallic oxide of high conductibility also has a little drift effect which may relate to material density. After long-term detection, it tends to stable response voltage and approximates to saturation, therefore, the TiO₂:Ru-based pH sensor has excellent performances and can apply to hard clam cultivated solutions properly.

 $\label{eq:table-interpolation} TABLE\ I$ Comparison of Solid-State Sensing Electrode for Drift Rate

Sensing film	Sample solution (pH)	Drift rate (mV/hour)	Standard deviation (mV/hour)	Reference
TiO ₂ :Ru	Cultivated solution (sample 1)	1.16	0.660	In this study
TiO ₂ :Ru	Cultivated solution (sample 2)	1.03	0.473	In this study
a-Si:H	1, 3, 5 and 7	1.08, 2.63, 4.83 and 6.53	N/A	[15]
a-WO ₃	7	15.7	N/A	[16]
ITO	6	6.11	N/A	[17]
SnO ₂	7	6.73	N/A	[17]

IV. CONCLUSION

We developed efficiently a ruthenium-doped titanium dioxide (TiO2:Ru) of high performance solid-state sensing electrode by co-sputtering system. The TiO₂:Ru-based sensing electrode is applied to measure for hydrogen ionic concentration in pH standard buffer solution and cultivated solutions. Surface images of TiO2:Ru film illustrate that the nano-crystallization appears cubic lattice, and it has good surface roughness and uniformity. Sensitivity and linearity of the TiO2:Ru-based sensing electrode are 55.20 mV/pH (S.D. =2.81 mV/pH) and 0.999 from pH1 to pH13, respectively. We presented the short-term and long-term response to determine the sensor's performance. Mean response voltages for short-term response between 41 seconds and 200 seconds in the cultivated solutions are -178.758 mV and -180.206 mV, respectively. Long-term drift of cultivated solutions (sample 1 and sample 2) are 1.16 mV/hour and 1.03 mV/hour, respectively. The experimental results demonstrate that the solid-state sensing electrode of ruthenium-doped titanium dioxide (TiO₂:Ru) is not only used to measure for water quality but also can be applied to pH measurement of hard clam cultivated solutions.

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Jung-Chuan Chou was born in Tainan, Taiwan, Republic of China, on July 13, 1954. He received the B.S. degree in physics from Kaohisung Normal College, Kaohsiung, Taiwan, in 1976; the M.S. degree in applied physics from Chung Yuan Christian University, Chung-Li, Taiwan, in 1979; and the Ph.D degree in electronics from National Chiao Tung University, Hsinchu, Taiwan, in 1988. He taught at Chung Yuan Christian University from 1979 to 1991. Since 1991 he has worked as an associate professor in the Department of Electronic Engineering at the National Yunlin University of Science and Technology. From 1997 to 2002 he was Dean, office of Technology Cooperation at the National Yunlin University of Science and Technology. And since 2002, he has been Secretary-General at the National Yunlin University of Science and Technology. His research interests are in the areas of amorphous materials and

devices, electrographic photoreceptor materials and devices, electronic materials and devices, sensor devices, and science education.

Cheng-Wei Chen was born in Pingtung, Taiwan, Republic of China, on February 3, 1983. He received Bachelor in the Department of Microelectronics Engineering from National Kaohsiung Marine University, Nanzih, Taiwan, in 2005. He has received the master degree in the Graduate School of Optoelectronics at National Yunlin University of Science and Technology, Douliou, Taiwan in 2007. He has pursued advanced study of the doctor degree in the Graduate School of Engineering Science and Technology at National Yunlin University of Science and Technology, Douliou, Taiwan since 2007. His research interests include material characterizations of biosensors, mainly of the separative gate field effect transistor sensor, semiconductor sensors and its applications.