Long-term Monitor of Seawater by using TiO$_2$: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 (TiO$_2$:Ru) is developed to measure hydrogen ion concentration in different cultivated solutions. Because the TiO$_2$:Ru sensing electrode has high chemical stability and superior sensing characteristics, thus it is applied as a pH sensor. Response voltages of TiO$_2$:Ru sensing electrode are readout by instrument amplifier in different sample solutions. Mean sensitivity and linearity of TiO$_2$:Ru sensing electrode are 55.20 mV/pH and 0.999 from pH1 to pH13, respectively. We expect that the TiO$_2$: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 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 (6CO$_2$+6H$_2$O $\rightarrow$ C$_6$H$_{12}$O$_6$+6O$_2$), fermentation (C$_6$H$_{12}$O$_6$+3CO$_2$ $\rightarrow$ 3CH$_4$+6CO$_2$), nitrification (NH$_4^+$+2O$_2$ $\rightarrow$ NO$_3^-$+H$_2$O+2H$^+$), oxysulfide (HS+2O$_2$ $\rightarrow$ SO$_4^{2-}$+H$^+$, sulfide reduction (C$_6$H$_{12}$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 ^{o}C and 32 ^{o}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 (TiO$_2$) 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 (SnO$_2$) and so on. In this investigation, we present a metallic modification for titanium dioxide (TiO$_2$) which decreases resistivity of TiO$_2$ sensing film, and increases carrier mobility for solid-state sensing electrode. Therefore, the ruthenium (Ru) ions are utilized to dope into TiO$_2$ 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). TiO$_2$ target and ruthenium target were purchased by Ultimate

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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 TiO_2:Ru sensing film

In this study, co-sputtering system is used to fabricate the ruthenium-doped titanium dioxide (TiO_2: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 TiO_2: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 TiO_2:Ru-based pH sensor. MOSFET (CD4007UB) is kept to work in linear region. Drain-Source voltage is set at 0.2V.
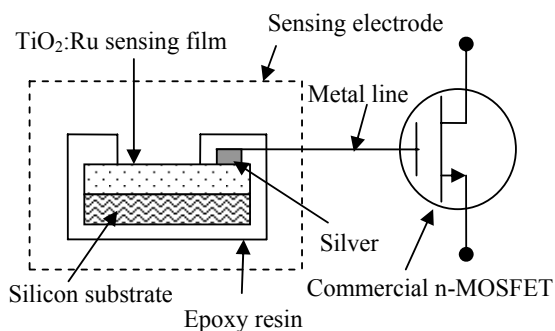

Fig. 1 Structure of TiO_2:Ru-based separative extended gate field effect transistor (SEGFET) is measured for I-V measurements

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 TiO_2:Ru sensing film, respectively. The TiO_2: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 TiO_2: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.
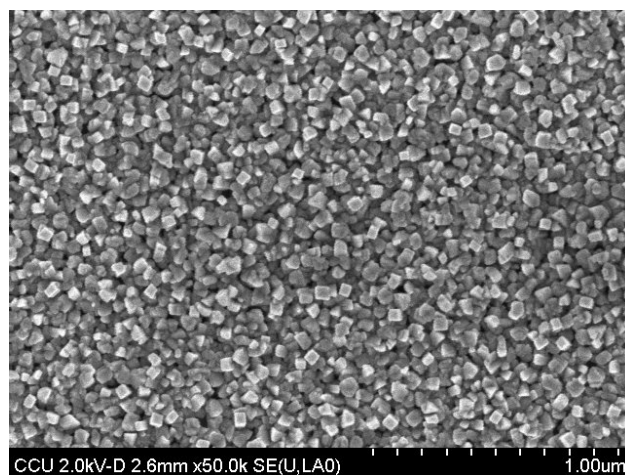
(a)
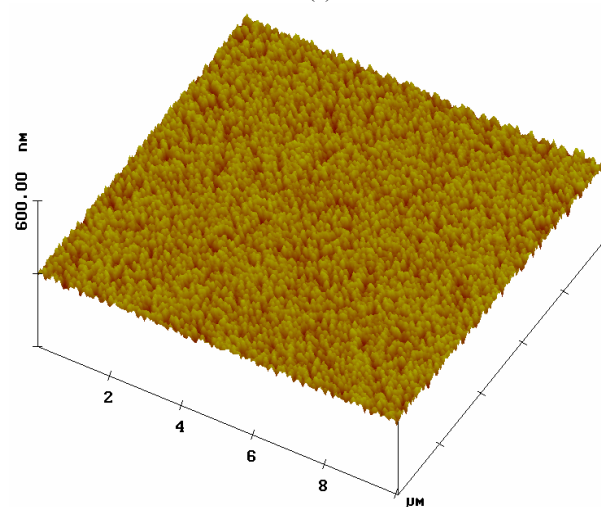
(b)

Fig. 2 (a) Surface morphology of TiO_2:Ru film is measured by FE-SEM; (b) Surface roughness of TiO_2:Ru film is measured by AFM

B. pH Sensing Characteristics of the TiO_2: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 (mV/ pH) of SEGFET sensor.

pH sensing performance for TiO$_2$:Ru-based SEGFET structure is defined. SEGFET is operated in non-saturation (linear) region which is as follows [12-15]:

$$I_D = K_n[2(V_{ref} - \Delta V_{TEG})V_{DS} - V_{DS}^2] \quad (1)$$

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 TiO$_2$:Ru SEGFET-based sensor are shown in Fig. 3(a) and Fig. 3(b), respectively. Sensitivity and linearity of the TiO$_2$: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 TiO$_2$: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.
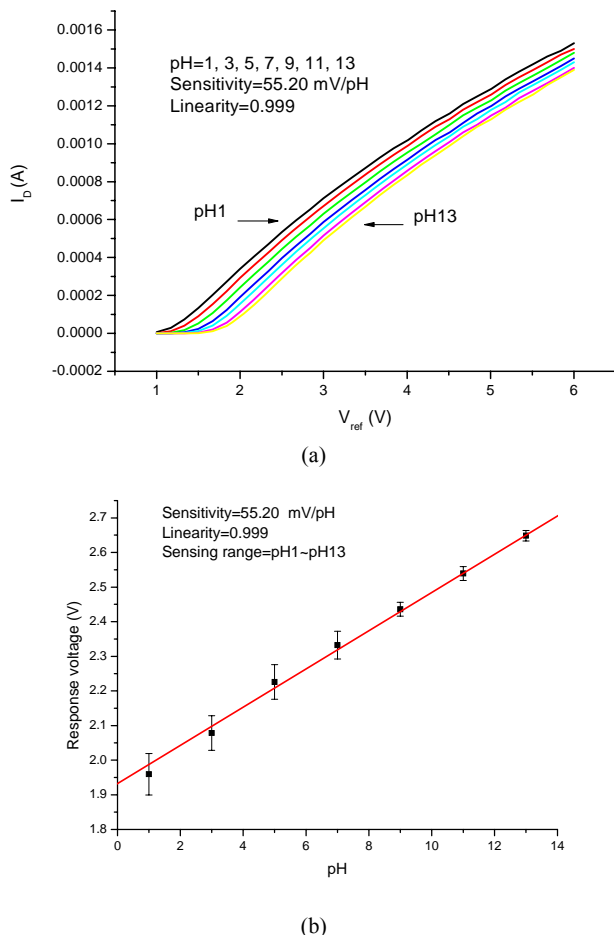

Interface between TiO$_2$:Ru-based solid-state sensing electrode and sample liquid has a reactive potentials, and its sensing mechanism is as follows [12-15]:

$$\phi^s - \phi^l = (\frac{1}{F})(\mu_{H^+}^l + \mu_{e^-}^s + \frac{\mu_O^s}{2} - \frac{\mu_{H_2O}^l}{2}) = constant + \frac{RT}{F}\ln a_{H^+}^l$$

$$-\frac{RT}{F}\ln a_0^s \quad (2)$$

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.
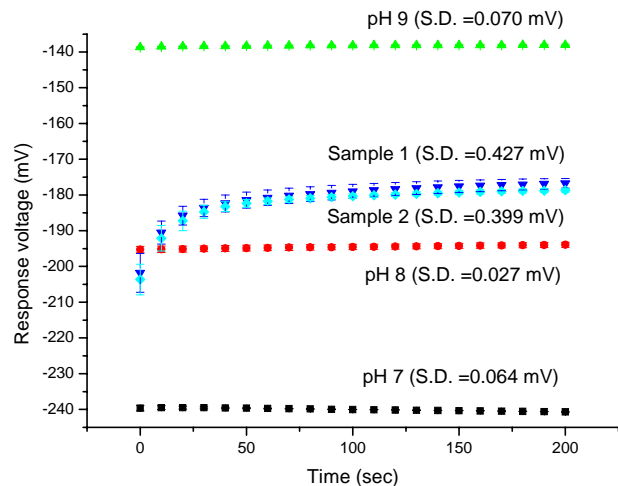

Fig. 4 Short-term responses for pH measurements of sample liquids are between 0 and 200 seconds

In order to provide for a based reference level and potential calibration, the TiO$_2$: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 TiO$_2$: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$^+$, Mg^{2+}, K$^+$

Fig. 3 (a) I-V curves of TiO$_2$:Ru-based SEGFET are measured from pH1 to pH13; (b) Sensitivity and linearity of TiO$_2$:Ru-based SEGFET are measured from pH1 to pH13

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 $25\pm0.1^{\circ}C$.

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]:

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

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 TiO$_2$:Ru-based pH sensor are exhibited in Fig. 5.
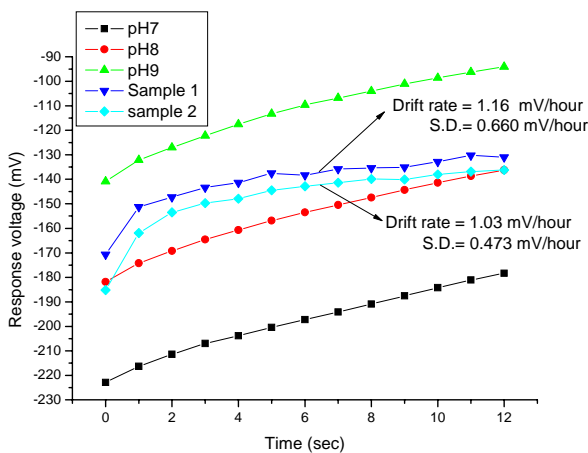

Fig. 5 Long-term responses for pH measurements of sample liquids are between 0 and 12 hours

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 TiO$_2$:Ru-based pH sensor has excellent performances and can apply to hard clam cultivated solutions properly.

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 (TiO$_2$:Ru) of high performance solid-state sensing electrode by co-sputtering system. The TiO$_2$:Ru-based sensing electrode is applied to measure for hydrogen ionic concentration in pH standard buffer solution and cultivated solutions. Surface images of TiO$_2$:Ru film illustrate that the nano-crystallization appears cubic lattice, and it has good surface roughness and uniformity. Sensitivity and linearity of the TiO$_2$: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 (TiO$_2$: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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