World Academy of Science, Engineering and Technology
International Journal of Electronics and Communication Engineering
Vol:3, No:5, 2009

Long-term Monitor of Seawater by using TiO_2:Ru Sensing Electrode for Hard Clam Cultivation

Jung-Chuan Chou, and Cheng-Wei Chen

Open Science Index, Electronics and Communication Engineering Vol:3, No:5, 2009 publications.waset.org/14756/pdf

***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 ($6CO_2+6H_2O \rightarrow C_6H_{12}O_6+6O_2$), 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 ($HS+2O_2 \rightarrow SO_4^{2-}+H^+$, sulfide reduction ($C_6H_{12}O_6+3SO_4^{2-}+3H^+ \rightarrow 6CO_2+3HS+6H_2O$) 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 ^oC and 32 ^oC, 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

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).

Open Science Index, Electronics and Communication Engineering Vol:3, No:5, 2009 publications.waset.org/14756/pdf

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.

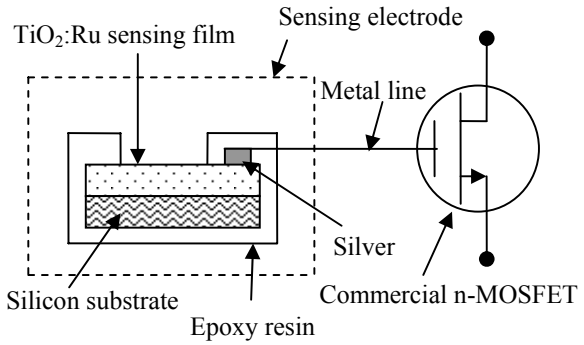
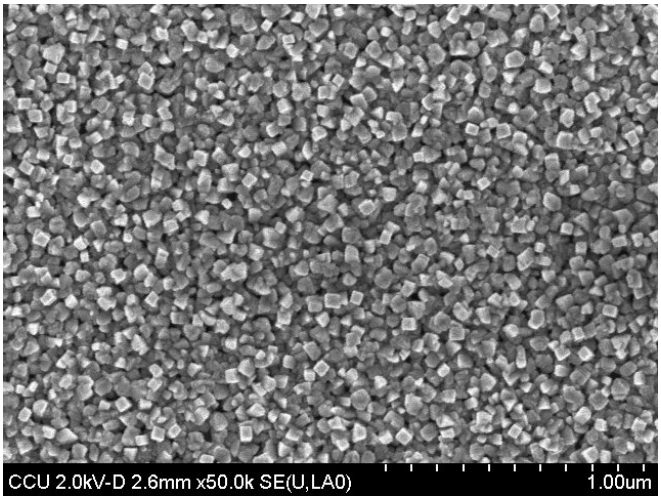


Fig. 1 Structure of TiO_2:Ru-based separative extended gate field effect transistor (SEGFET) is measured for I-V measurements

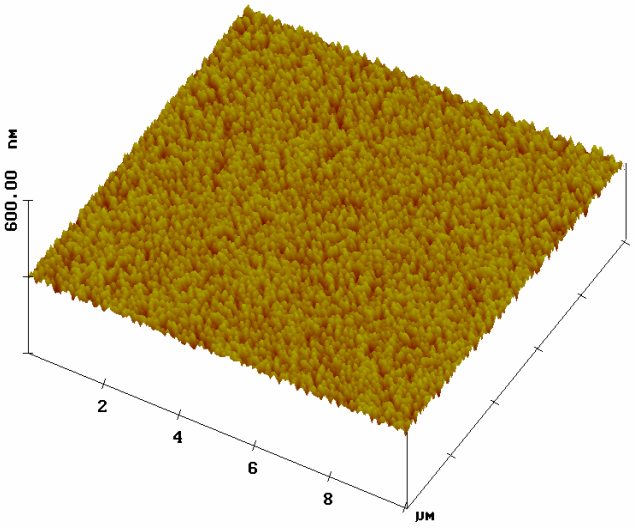
III. Results and Discussion

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

Open Science Index, Electronics and Communication Engineering Vol:3, No:5, 2009 publications.waset.org/14756/pdf

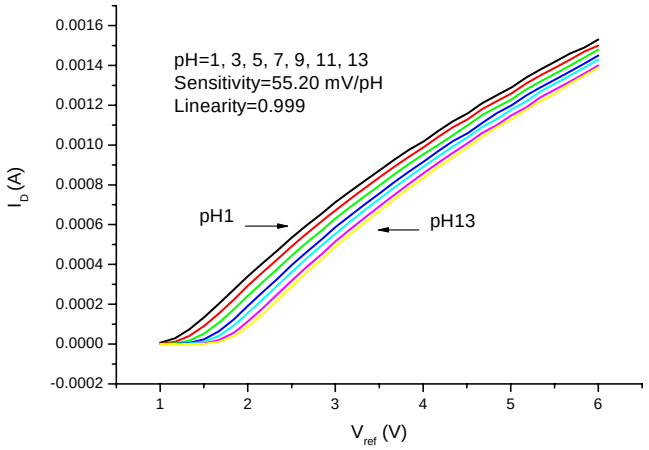
Measure Unit). Measurement data are analyzed by Origin Pro. 7.0 software, and then we can obtain sensitivity (□mV/□pH) of SEGFET sensor.

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]:

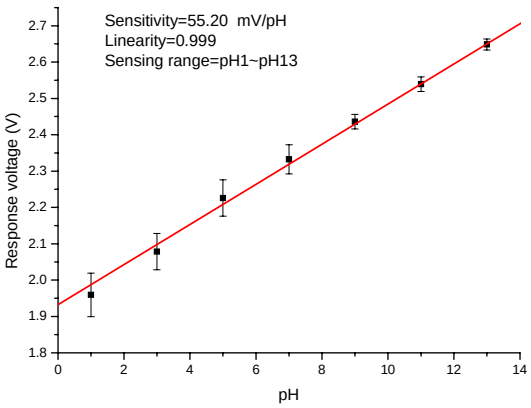
$$I_D = K_n[2(V_{ref} - \Delta V_{TEG})V_{DS} - V_{DS}^2] \quad (1)$$

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.



(a)



(b)

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

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]:

$$\phi^s - \phi^l = (\frac{1}{F})(\mu^l_{H^+} + \mu^s_{e^-} + \frac{\mu^s_O}{2} - \frac{\mu^l_{H_2O}}{2}) = \text{constant} + \frac{RT}{F}\ln a^l_{H^+} - \frac{RT}{F}\ln a^s_0 \quad (2)$$

where the $\mu^s_{e^-}$ 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, $a^l_{H^+}$ and a^s_0 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.

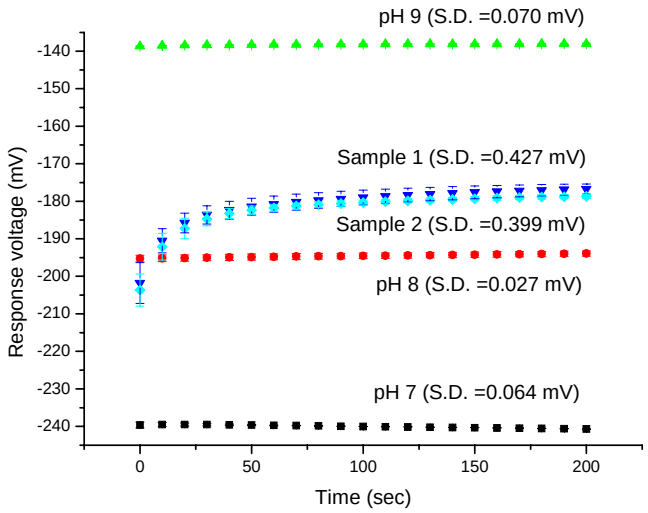


Fig. 4 Short-term responses for pH measurements of sample liquids are between 0 and 200 seconds

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^+

Open Science Index, Electronics and Communication Engineering Vol:3, No:5, 2009 publications.waset.org/14756/pdf

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]:

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

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 ΔO/Δt is the drift of sensor. ΔO/Δt 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.

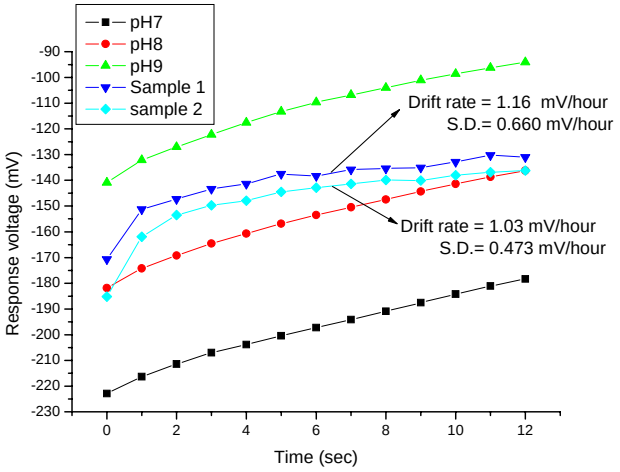


Fig. 5 Long-term responses for pH measurements of sample liquids are between 0 and 12 hours

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.

ACKNOWLEDGMENT

This study is supported by National Science Council, The Republic of China, under the contract NSC 97-2221-E-224-058 -MY3, 96-2628-E-224-008-MY3 and NSC 97-2221-E-224 -059.

Open Science Index, Electronics and Communication Engineering Vol:3, No:5, 2009 publications.waset.org/14756/pdf

REFERENCES

[1] S. P. Hong, D. S. Kim and Y. M. Kim, "Effect of water temperature, salt and MgCl2 concentration on sand ejection characteristics of short neck clam" Bull. Kor. Fish. Soc., vol. 30, pp. 114-118, 1997.

[2] Y. Saito, T. Suzuki, K.I. Kobayashi, K. Sato, M. Hirafuji, T. Fukatsu, R. Ichimura, R. Yashiro, S. Takeuchi, K. Yuasa, S. Watanabe, F. Kobayashi, T. Kawahara and T. Kameoka, "Field server monitoring system for construction of IT farming and agri-tourism - trial report from Obuse-town, Nagano Japan," Proceedings of the International Joint Conf. on SICE-ICASE, pp. 4848-4851, 2006.

[3] G. Dalmin, K. Kathiresan and A. Purushothaman, "Effect of probiotics on bacterial population and health status of shrimp in culture pond ecosystem," Ind. J. Experimental Biology vol. 39(9), pp. 939-942, 2001.

[4] Y.C. Lee, "The study on the accumulation of anaerobic end products in various tissues of hard clam," Master's thesis, Nat. Chiayi Univ., Taiwan, 2008.

[5] A.C. Lee, Y.H. Lin, C.R. Lin, M.C. Lee, and Y.P. Chen, "Effects of components in seawater on the digging behavior of the hard clam (Meretrix lusoria)," Aquaculture, vol. 272, pp. 636-643, 2007.

[6] M. Z. Atashbar, "Nano-sized TiO2 thin film for alcohol sensing application," Maui, Hawaii, Proc. IEEE Conf. on Nanotech., pp. 544-549, 2001.

[7] C. Podaru, V. Avramescu, R. Enache, and G. Stoica, "TiO2 anodic oxide films for oxygen gas sensors," Proc. IEEE Semiconductor Conf., vol.2, pp. 565-568, 1998..

[8] T. Torimoto, Y. Okawa, N. Takeda, and H. Yoneyama, "Effect of activated carbon content in TiO2-loaded activated carbon on photodegradation behaviors of dichloromethane," J. Photochem. Photobiology. A, Chem., vol. 103, pp. 153-157, 1997.

[9] J. Matos, J. Laine and J.M. Herrmann, "Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon," Appl. Catalysis B: Environ., vol. 18, pp. 281-291, 1998.

[10] L. Cesar, A. Kay, J. A. G. Martinez and M. J. Gratzel, "Translucent thin film Fe2O3 photoanodes for efficient water splitting by sunlight: nanostructure-directing," J. Amer. Chem. Soc. Vol. 128, pp. 4582-4583, 2006.

[11] S. F. Chen, L. Chen, S. Cao and G. Y. Cao, "The preparation of nitrogen-doped photocatalyst TiO2−xNx by ball milling," Chem. Phys. Lett., vol. 413, pp. 404-409, 2005.

[12] P. Woias, L. Meixner and P. Fröstl, "Slow pH response effects of silicon nitride ISFET sensors," Sens. Actuators B, vol. 48, pp. 501-504, 1998..

[13] L. Bousse, D. Hafeman and N. Tran, "Time-dependence of the chemical response of silicon nitride surfaces," Sens. Actuators B, vol. 1, pp. 361-367, 1990.

[14] D. Yu, Y. D. Wei and G. H. Wang, "Time-dependent response characteristics of pH-sensitive ISFET," Sens. Actuators B vol. 3, pp. 279-285, 1991.

[15] J.C. Chou, H.M. Tsai, C.N. Shiao, and J.S. Lin, "Study and simulation of the drift behaviour of hydrogenated amorphous silicon gate pH-ISFET," Sens. Actuators B, vol. 62, pp. 97-101, 2000.

[16] J.L. Chiang, S.S. Jan, J.C. Chou and Y.Y. Chen, "Study on the temperature effect, hysteresis and drift of pH-ISFET devices based on amorphous tungsten oxide," Sens. Actuators B, vol. 76, pp.624-628, 2001.

[17] L.T. Yin, J.C. Chou, W.Y. Chung, T.P. Sun and S.K. Hsiung, "Separate structure extended gate H+-ion sensitive field effect transistor on a glass substrate," Sens. Actuators B 71, 106-111, 2000.

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.