Characterization of Nanopores on Micropillars Pt Electrodes for Non-Enzymatic Electrochemical Sensor Applications

Dae Joon Park, Yi Jae Lee, and Jae Yeong Park

Abstract—**In this paper, mesoporous Pt on micro pillars Pt electrode is newly designed, fabricated, and characterized on silicon substrate for non-enzymatic electrochemical sensor micro-chip integrated with CMOS readout circuitry. The fabricated micro/nano Pt electrode has cylindrical hexangular arrayed nano Pt pores with a diameter of 3.2 nm which is formed on top of the micro pillars Pt electrode with approximately 6μm in diameter, 6μm in space, and 50 μm in height. The measured current responses of the fabricated plane Pt, mesoporous Pt, and mesoporous Pt on the micro pillar Pt electrodes are approximately 9.9 nA/mm^2, 6.72 μA/mm^2, and 7.67 μA/mm^2 in 10mM glucose solution with 0.1M phosphate buffered saline (PBS) solution, respectively. In addition, the measured current responses of the fabricated plane Pt, mesoporous Pt, and mesoporous Pt on the micro pillar Pt electrodes are approximately 0.15 μA/mm^2, 0.56 μA/mm^2, and 0.74 μA/mm^2 in 0.1mM ascorbic acid (AA) solution with 0.1M phosphate buffered saline (PBS) solution, respectively. This experimental results show that the proposed micro/nano Pt electrode is highly sensitive and promising for CMOS integrated non-enzymatic electrochemical sensor applications. Since the micro-pillar Pt electrode can also be utilized with a micro-fluidic mixer in the sensor chip, the sensor chip can be much smaller, cheaper, and easier to be fabricated.**

Index Terms—**Mesoporous Pt, Micropillar Pt, Electrochemical sensor, CMOS integrated, Non-enzymatic, Biosensors, Glucose sensors**

I. INTRODUCTION

Micro-bio chips have actively been researched for genetics, proteomics, cellomics, and clinical/forensic analyses, since they can provide high-throughput and possibly on-site solutions, from sample preparation (e.g. sample collection, concentration, extraction and purification) and biochemical reactions (e.g. immunological reactions, enzymatic reactions and DNA assays) to signal detection (optical or electrochemical) on a single chip [1].

Most of electrochemical bio chips use enzymes and mediators in their sensing electrodes to increase responding signals in a short period of time. However, these enzymes are not repeatable in fabrication and stable at thermal and chemical environment during storage and use. In addition, they are highly costive and disposable. To overcome these drawbacks, non-enzymatic sensing electrodes with high sensitivity and their miniaturization are necessary. The mesoporous (nanopores with sizes of 2 nm ~ 50 nm) platinum formed on a bulky Pt rod was reported for non-enzymatic glucose sensor applications [2]. Glucose was very sensitively reacted in the mesoporous Pt working electrode, due to the extremely expanded surface activation area of the working electrode. In addition, ascorbic acid (AA) and acetaminophen (AP) in human blood are much less sensitively reacted than the glucose. Since the diameter of the nanopores is smaller than the scale of the chronoamperometric diffusion field and the diffusion layer reaches several micrometers away from the sensing electrode surface, the reactants

Manuscript received . Jun. 05, 2007 ; revised Aug. 21, 2007.
Department of Electronic Engineering, Kwangwoon University, Seoul, Korea.
E-mail: jaepark@kw.ac.kr

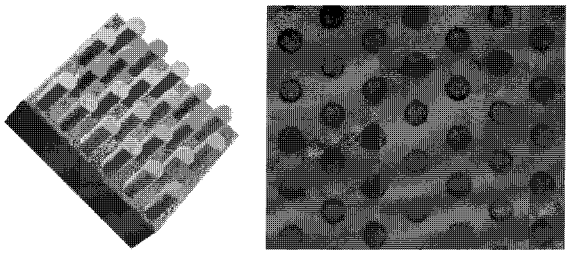
are depleted very quickly in the mesoporous electrode [3]. The geometrical structure and fabrication method of the mesoporous Pt electrode were first reported in 1997 [4]. The mesoporous Pt electrode was comprised of cylindrical hexangular arrayed pores with a diameter of 2.5 nm and 5 nm of a spacing distance between the nano pores.

In this paper, new geometry and fabrication method are proposed to fabricate the non-enzymetic sensing electrode with high sensitivity which can also be used as micropillars to mix fluids well at the micro-bio chips. The sensitivity can be extremely increased by enlarging the reactivation surface area of the sensing electrode by combining the mesoporous Pt and the micropillars Pt electrodes. The fabricated micro-nano electrodes are evaluated in glucose solutions to check its usability for non-enzymatic glucose chip integrated with CMOS readout circuitry.

II. FABRICATION

The mesoporous Pt electrode was previously fabricated on silicon substrate for non-enzymatic CMOS integrated electrochemical sensor applications [5]. First, 42%(w/w) C16EO8 (octaethylene glycol monohexadecyl ether, 98% purity, Fluka), 29% (w/w) distilled water (18 MΩ cm) and 29% (w/w) HCPA (hexachloroplatinic acid hydrate, 99.9% purity, Aldrich) are well mixed in a beaker and heated up to 85℃, at which the mixture becomes transparent and homogeneous. A silicon piece sputtered with platinum film is inserted into the mixture and the temperature was lowered down to 25℃. At this step, the liquid crystalline hexagonal structure is formed on top of the sputtered Pt film deposited on the silicon substrate. And then, Pt ions are electroplated into the hexagonally packed cylindrical nano-molds by applying constant potential (-0.12V vs. Ag/AgCl). After soaking the sample in distilled water for several hours to remove the $C_{16}EO_8$, the mesoporous Pt electrode is finally formed by cycling the sample in 2M sulfuric acid solution at between +1.2 and -0.4 V vs. Ag/AgCl.

The micro pillar Pt electrodes with approximately 6 μm in diameter and 50 μm in height are fabricated by using deep RIE silicon etcher and DC sputtering system. The micro pillars have the same spacings as their diameters.



(a) (b)

Fig. 1. Schematic drawing (a) and microphotograph (b) of the micro pillar Pt electrode formed on silicon substrate.

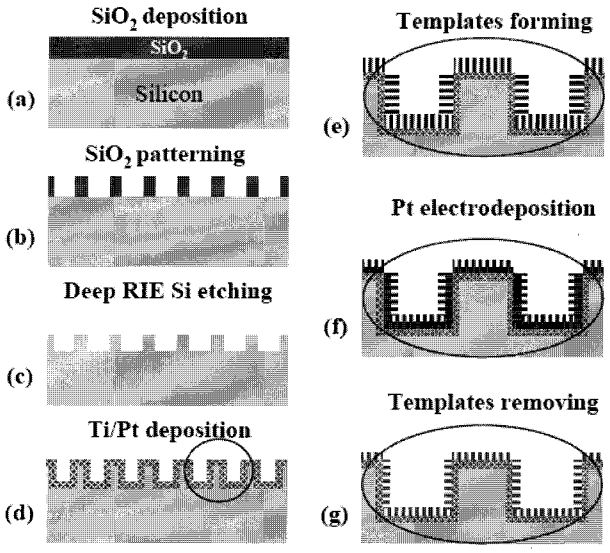


Fig. 2. Fabrication steps of the mesoporous Pt on the micro pillar Pt electrode; (a) SiO_2 deposition, (b) Patterning and SiO_2 etching, (c) Si deep RIE etching, (d) Ti/Pt deposition, (e) Forming of surfactant templates, (f) Electrodeposition of mesoporous Pt , (g) Remval of surfactant templates.

Fig. 1 (a) and (b) show a schematic drawing and a photomicrograph of the micro-pillar Pt electrode. The fabrication steps of the mesoporous Pt on the micro-pillar Pt electrode are represented in Fig. 2. The SiO_2 layer was firstly deposited and patterned on a high resistivity silicon substrate. The micro pillar structure was fabricated by using deep RIE silicon etcher and SiO_2 mask layer was removed by wet etching technique. Platinum was deposited on the formed micro pillars by using DC sputtering system. Hexagonal liquid crystal templates of the $C_{16}EO_8$ are formed and Pt ions are electrodeposited on the formed micro pillar Pt electrode. Finally, the nano-templates are clearly removed in the deionized water.

III. Experimental Results and Discussions

All electrochemical measurements were performed in three electrodes system by using an electrochemical analyzer (CH Instruments Inc., USA) and an Ag/AgCl electrode and a plane Pt electrode were used as a reference electrode and a counter electrode, respectively.

For evaluation of the fabricated mesoporous Pt on the micro pillar Pt electrode, the electrical current responses were measured and compared. Fig. 3 shows cyclic voltammetry in 2M sulfuric acid solution of the fabricated micro and nano Pt electrodes. This experiment was performed to clean the surface and to activate the electrodes by using hydrogen adsorption/desorption methods [6]. The current response of the mesoporous Pt on the micro pillar Pt electrode is larger than the other Pt electrodes. The cyclic voltammetric responses were measured in 10mM potassium ferricyanide solution [7].

Fig. 4 shows cyclic voltammetric responses of the fabricated Pt electrodes in 10 mM $K_3Fe(CN)_6$ with 3M KCl solution at scan rate 100 mV/sec. This result also shows the same tendency as the sulfuric acid solution. Fig. 5 shows chronoamperometric responses of the fabricated Pt electrodes in 2mM hydrogen peroxide with 0.1M phosphate buffered saline (PBS) solution. Hydrogen peroxide is an oxidized substance of glucose and its concentration is closely associated with that of the glucose concentration. As shown in Fig. 5, the current response of the mesoporous Pt on the micro pillar electrode is much larger than the other Pt electrodes. This data indicates that the mesoporous Pt on the micro pillar Pt electrode is very sensitive to the hydrogen peroxide and other chemicals, and strongly applicable for the electrochemical analysis micro-systems and LOC applications.

Fig. 6 shows the measured current responses of the fabricated Pt electrodes at various glucose concentrations. This data was obtained by measuring the chronoamperometric responses to various concentration of glucose at 60 sec. The current responses of the fabricated plane Pt electrode, mesoporous Pt electrode, and mesoporous Pt on micro pillar electrode are approximately 0.14 $\mu A/mm^2$, 6.72 $\mu A/mm^2$, and 7.67 $\mu A/mm^2$ in 10mM glucose solution without stirring, respectively. This data indicates that the mesoporous Pt on the micro pillar electrode is much more sensitive than the other Pt electrode to glucose solution.

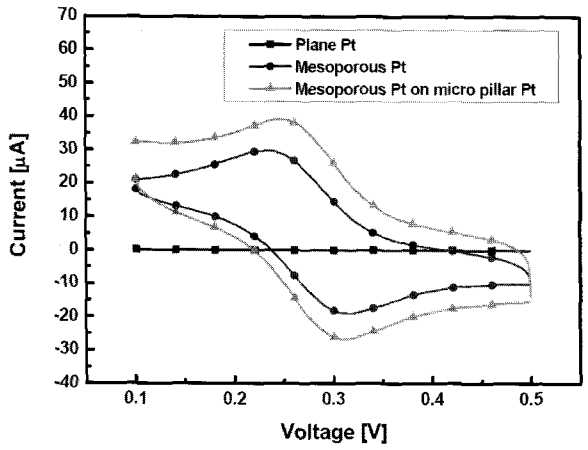


Fig. 3. Cyclic voltammetric responses of the fabricated plane Pt, mesoporous Pt, and mesoporous Pt on micro pillar Pt electrodes in 10mM K3Fe(CN)6 with 3M KCl solution at scan rate 100 mV/sec.

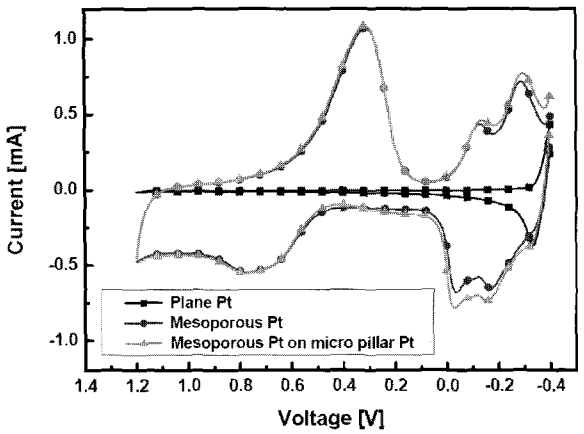


Fig. 4. Cyclic voltammetry of the fabricated plane Pt, mesoporous Pt, and mesoporous Pt on micro pillar Pt electrodes in 2M sulfuric acid solution.

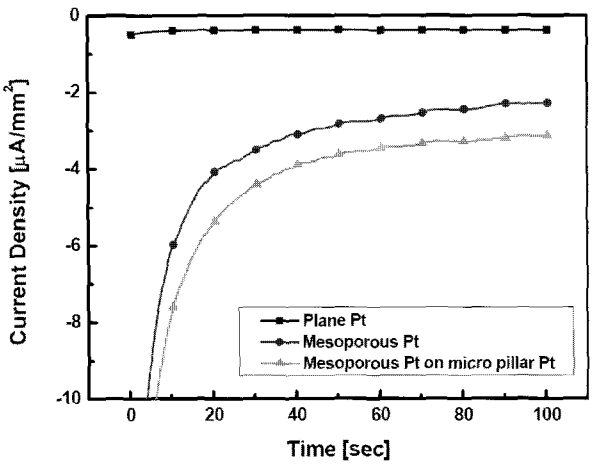


Fig. 5. Linear sweep voltammetry of the fabricated plane Pt, mesoporous Pt, and mesoporous Pt on micro pillar Pt electrodes in 2mM hydrogen peroxide solution with 0.1M PBS solution.

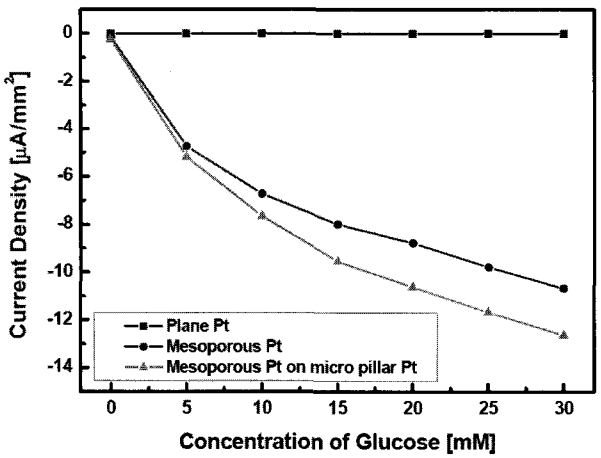


Fig. 6. Current response of the fabricated plane Pt, mesoporous Pt, and mesoporous Pt on micro pillar Pt electrodes at various glucose concentrations with 0.1M PBS solution.

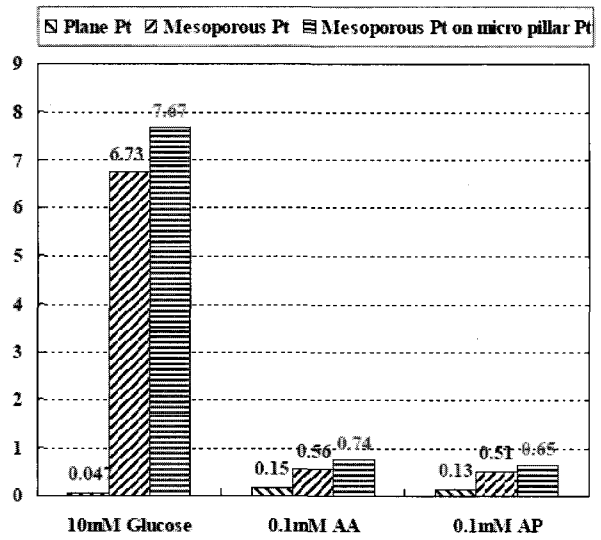


Fig. 7. Current responses of the fabricated plane Pt, mesoporous Pt, and mesoporous Pt on micro pillar Pt electrodes in (a) 10mM glucose solution with 0.1 M PBS solution, (b) 0.1mM AA solution with 0.1 M PBS solution, (c) 0.2mM AP solution with 0.1 M PBS solution. [unit : μA]

Fig. 7 shows a comparison of the current response of the fabricated Pt electrodes in 0.1 M PBS solutions mixed with 10 mM glucose solution, 0.1 mM ascorbic acid (AA) solution, and 0.2 mM acetaminophen (AP) solution. As shown in Fig. 7, the current responses are much larger than that of the plane Pt electrode at the glucose solution, while the current responses of the mesoporous Pt electrode and the mesoporous Pt on the micro pillar electrode are smaller than that of the plane Pt electrode at the AA and AP solutions. It shows that the fabricated mesoporous Pt electrode and mesoporous Pt on the micro pillar electrode are hardly influenced by AA and AP unlike the plane Pt electrode. These data shows that the proposed micro/nano Pt electrode is promising to the development of non-enzymetic and continuous monitoring biosensor chips integrated with CMOS read out circuits for ubiquitous health care and diagnosis systems.

IV. Conclusions

Mesoporous Pt combined with micro-pillar arrayed Pt electrode has been fabricated and characterized on silicon substrate in order to develop the highly sensitive and non-enzymetic sensing electrochemical sensor chips integrated with CMOS read out circuits. In cyclic voltammetric responses, the mesoporous Pt on the micro pillar Pt electrode showed much better performance characteristics than the purely mesoporous Pt electrode due to the largely expanded surface area. The measured current responses were also large enough to analyze the chemical substances without any enzymes. And also, the experimental results in AA and AP solution showed that the strong potential of the fabricated mesoporous Pt on the micro pillar Pt electrode for non-enzymatic glucose sensor chip integrated with CMOS circuitry. Bio chips can also be miniaturized, simplified, and easily fabricated by utilizing the micro pillar electrode as the mixer of the bio chips.

Acknowledgments

This research was supported by the Korea Ministry of Information and Communication as a supporting project to form a Foundation of Advanced Leading Technology. The authors acknowledge MiNDaP group members for their technical supports and discussions.

References

[1] Wen-Tso Liu and Liang Zhu, "Environmental microbiology-on-a-chip and its future impacts," *TRENDS in Biotechnology*, vol. 23 (4), pp. 174-179, April 2005.

[2] S. J. Park, T. D. Chung and H. C. Kim, "Nonenzymatic

glucose detection using mesoporous platinum," *Anal. Chem. United States*, vol. 75, pp. 3046-3049, July 2003.

[3] S. Park, H. Boo and T. D. Chung, "Elecrochemical non-enzymatic glucose sensors," *Anal. Chim. Acta.*, vol. 556, pp. 46-57, 2006.

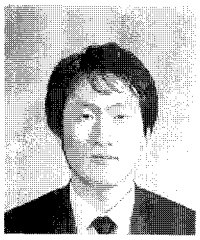
[4] G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen and J. H. Wang, "Mesoporous platinum films from lyotropic liquid crystalline phases," *Science. United States*, vol. 278, pp. 838-840, October 1997.

[5] H. K. Seo and J. Y. Park, "Nano-Fabricated Mesoporous Pt electrode on Silicon for CMOS Integrated Electrochemical Sensor Applications", *IEEE NEMS* 2006.

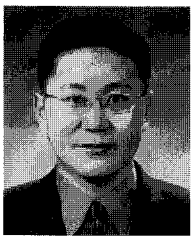
[6] H. Boo, S. Park, B. Ku, Y. Kim, J. H. Park, H. C. Kim and T. D. Chung, "Ionic strength-controlled virtual area of mesoporous platinum electrode," J. *Am. Chem. Soc. United States*, vol. 126, pp. 4524-4525, March 2004.

[7] Daniel C. Harris, "Quantitative Chemical Analysis," *W. H. Freeman and Company*. New York, Sixth edition, 2003.

Dae Joon Park was born in Seoul, Korea, in 1982. He has received his B.S degree in 2006 from Department of Electronic Engineering, Kwangwoon University, Seoul, Korea. His research area is to develop CMOS-compatible non-enzymatic glucose sensors and their packaging technologies for in-vitro and in-vivo applications.



Yi Jae Lee was born in Seoul, Korea in 1980. He has received his B.S degree in 2006 from Department of Electronic Engineering, Kwangwoon University, Seoul, Korea. His research area is to develop non-enzymatic glucose and cholesterol sensors for micro-TAS and methanol sensors for fuel cell applications.



Jae Yeong Park received his B.S degree in Telecommuniation Enginnering from Korea Aerospace University in 1992. He received M.S.E.E and Ph.D. degree in Electrical and Computer Engineering from Georgia Institute of Technology in 1995 and 1997, respectively. After graduation, he worked at the Packaging Research Center of Georgia Institute of Technology as a research engineer for 2 years. He has also worked at Microsystem group in LG Electronics Institute of Technology as a Team leader of RF MEMS research for 6 years. In September 2004, he joined the faculty of the department of Electronics Engineering in Kwangwoon University in Seoul Korea. He has published more than 130 journal articles and conference proceedings and filed more than 85 patents. His current research interests include microelectromechanical systems (MEMS, microactuators for optical and RF applications, micro-packaging (wafer level packaging, SOP, SOC, multichip modules), non-enzymatic electrochemical sensors, smart dust, and RF MEMS components (mechanical RF switches, tunable capacitors, micro-resonators, micro-antennas for multi band/mode applications, integrated phase shifter, TFBAR filters/duplexers, oscillators, micro high Q inductors/ transformers, balun/power dividers, tunable filters, MEMS based VCO/PAM, RF FEM (front-end module)).