DEVELOPMENT AND CHARACTERIZATION OF ELECTROCHEMICAL CANTILEVER SENSOR FOR BIO/CHEMICAL SENSING APPLICATIONS

Xueling Quan*, Lee M. Fischer, Anja Boisen, Maria Tenje

Technical University of Denmark, DTU Nanotech – Department of Micro- and Nanotechnology, Denmark

ABSTRACT

We report the improvements made to our previously developed electrochemical cantilever (EC) sensor, where nanoporous gold material is employed as working electrodes in microcantilever arrays, while combined counter-reference electrodes are integrated on the chip. For a surface stress change of 1mN/m induced on the microcantilever, the cantilever deflects is 7.3 nm at the free end, indicating high sensitivity to surface stress changes. The results suggest that the performance of the electrochemical cell is stable. A much enhanced sensitivity in surface chemistry-driven actuation can be achieved by using nanoporous gold with a high-surface area to volume ratio.

KEYWORDS: Cantilever, Electrochemistry, Cyclic Voltammetry, Nanoporous Gold

INTRODUCTION

Combining electrochemistry with microcantilevers provides a potentially powerful platform for biological and chemical sensing. In these sensors, the extreme sensitivity to surface stress change of the microcantilever is combined with the electrochemical techniques. Examples including dopamine oxidation [1], electrochemically-induced surface stress [2] and underpotential metal deposition [3] have been investigated. Increasing the active surface area of working electrodes will improve the sensitivity of sensors. Nanoporous gold with very high surface area to volume ratio is an attractive candidate for electrodes [4] and a macroscopic surface-chemistry-induced change of the surface stress responded in nanoporous gold can be achieved in an electrochemical environment [5]. For these reasons, there are currently many interests in developing nanoporous gold as electrochemical electrodes. In this work, we fabricated the nanoporous gold (np-Au) electrodes on the cantilever chip as the working electrodes, reference electrode and counter electrode for the standard electrochemical cell. Performance of nanoporous gold electrochemical cantilever chip with the static cantilever detection and electrochemical techniques in the sensing abilities is investigated.

CANTILEVER THEORY

For surface stress sensing, when the chemical or biological event happens on the surface of cantilever, the surface stress difference is induced between the activated and passive surface. The surface stress can be calculated by Stoney's formula [6], as follow

$$\Delta\sigma = \sigma_1 - \sigma_2 = \frac{Et^2}{6R(1-\upsilon)} \qquad (1)$$

Where σ_1 and σ_2 are the surface stresses applied to the top and bottom surfaces of the substrate, respectively, E is the substrate's Young's modulus, t is its thickness, R is the substrate's radius of curvature, and v is the Poisson's ratio.

EXPERIMENTAL

We fabricated the chips using standard cleanroom methods. The main steps of the np-Au electrodes fabrication process are illustrated in Figure 1 a-d. Silicon (100) wafers (100 mm diameter) were used as the substrate, while gold (99.99%), silver (99.99%) and chromium (99.99%) were employed as the sputtering targets. First, a 500 nm insulating layer of Si_3N_4 was deposited by LPCVD. The cantilever array (frontside) and body chip (frontside and backside) were patterned using UV photolithography, then reactive ion etched (RIE) through the entire depth of the silicon nitride to reach the substrate (Figure 1b). After using optimized sputtering/co-sputtering process to deposit the metal layers (Cr/Au/AgAu) [7], the electrodes pattern were created by lift off processing (Figure 1 c). Finally, the cantilevers were released in heated potassium hydroxide (KOH, 500 g/l, 80 °C) (Figure 1 d). The np-Au electrodes were obtained from AgAu alloys by chemical dealloying at room temperature. Figure 1e (top) shows a SEM image of a np-Au sample and Figure 1e (bottom) shows a photograph of finished electrochemical-cantilever chip, in which the six cantilever electrodes and two reference/counter electrodes are clearly visible.

To characterize the stability of the sensor, cyclic voltammetry was performed in solutions of different $[Fe(CN)_6]^{3-/4-}$ redox couple concentrations. A previously-developed electrochemical cantilever platform with flow control [8] was applied in this work (as shown in Figure 2). This platform makes it possible to readout the optical deflection of cantilever and electrochemical signal simultaneously. Cyclic voltammetry was performed between potentials of -0.4 V and 0.4 V (versus a np-Au pseudo-reference) with a 0.1 V/s scan rate. The voltammetry was performed using the np-Au working electrode surface of the active microcantilever, in a 0.2M KNO_3 supporting electrolyte without/with 2 mM, 1mM, 500 µM, 100 µM, 50 µM of $[Fe (CN)_6]^{3-/4-}$ couple. The controllable flow allows to keep the diffusion layer thickness steady, as well as to avoid the influence induced by the flow on the mechanical behavior of microcantilever. The deflection of cantilever was measured using the optical lever method, and converted to surface stress using Stoney's formula [6].

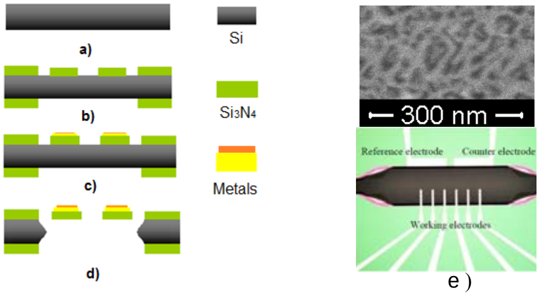


Figure 1: Fabrication process of electrochemical cantilever sensor: a) a Si substrate, b) SiN Cantilever pattern by Lithography and wet etching, c) metal layers deposition and patterning by lift off, d) Cantilever releasing by KOH etching, e) photograph of the fabricated device (bottom) and SEM image of nanoporous gold (top).

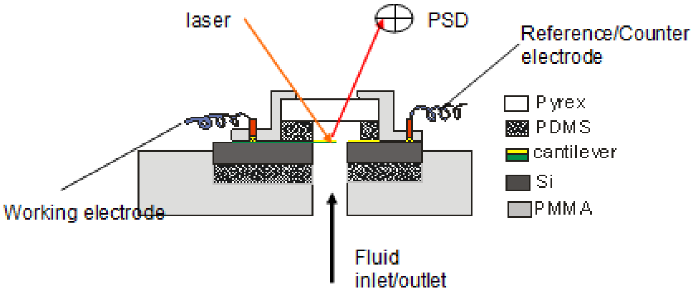
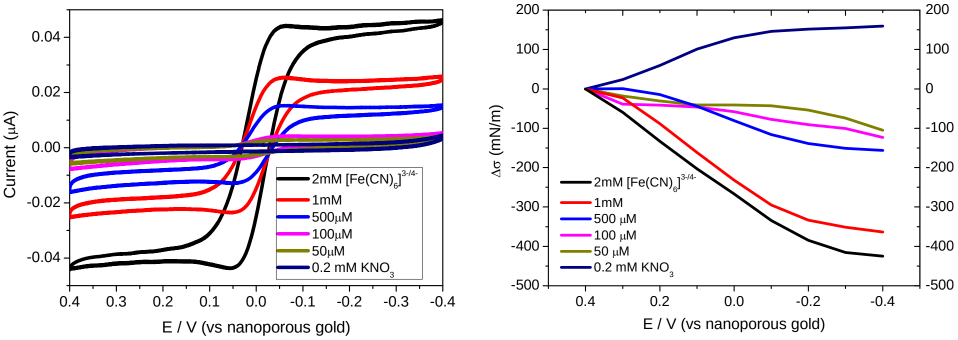


Figure 2: The schematic illustration of electro-chemical cantilever platform.



(a) (b)

Figure 3: (a) Cyclic voltammograms of current–potential responses in KNO_3 electrolytes without/with 50 μM, 100 μM, 500 μM, 1mM and 2mM concentrations of $[Fe(CN)_6]^{3-/4-}$ redox couple, respectively. (b) Corresponding Surface stress changes are plotted versus potential from 0.4 V to -0.4 V for a cantilever in the KNO_3 electrolytes without/with various concentrations of $[Fe(CN)_6]^{3-/4-}$ redox couple.

RESULTS AND DISCUSSION

Figure 3a shows the current–potential response during cycling, where the current peak grows gradually without shift in peak potential, when the concentration of $[Fe(CN)_6]^{3-/4-}$ couple increases from 50 µM to 2 mM. These results indicate that the performance of the electrochemical cell is stable. As shown in Figure 3b, the surface stress change is recorded simultaneously during the potential scanning from 0.4 V to -0.4V. In the KNO_3 electrolyte solution without any electroactive species, during the cathodic sweep, the surface stress increases as the potential decreases, and this corresponds to an increasing tensile stress on the nanoporous gold surface in agreement with those reported by Godin *et al.* [2] and Weigend *et al.* [9]. An opposite behavior is observed in the solution with $[Fe(CN)_6]^{3-/4-}$ redox couple, i.e. compressive stress on the nanoporous gold surface increases as the potential decreases, as a result of the occurring electrochemical reactions. It is known that the surface stress change observed in pure electrolyte during cycling is mainly ascribed to the external potential actuation and electrochemically-driven adsorption of ions on metal electrodes [10]. However, the results obtained in solution with the redox couple during the cathodic sweeping reveal that the electrons transferred from electrode to the solution also could lead to a change in surface stress, which shown an opposite behavior compared with that induced by the ions adsorption. Additionally, it is found that the total electron energy increases with increasing of the concentration of redox couple, resulting in increasing of the surface stress change as well. Meanwhile, because of larger surface to volume ratio in the nanoporous gold, the transferred electron density from the nanoporous gold electrode can be increased compared with that from the flat gold electrode with the same footprint area.

CONCLUSION

Our previously-developed electrochemical-cantilever sensor has been modified with nanoporous gold electrodes, and the electromechanical behavior of the resulting devices was characterized. The direction of cantilever deflection is observed to be downwards when performing a cathodic sweep in $[Fe(CN)_6]^{3-/4-}$ ($\Delta\sigma < 0$), and upwards during a same potential sweep in KNO_3 ($\Delta\sigma > 0$). The magnitude of the potential-dependent surface stress is observed to be dependent on the concentration of the redox couple presents in the solution, with a larger stress magnitude occurring in more concentrated solutions. The results indicate that the electrochemical cantilever sensor is very sensitive to the chemical events happening on the surface of cantilever. The nanoporous gold exhibits a promising tendency to a much enhanced sensitivity, which has a great potential to be used in electrochemical applications.

ACKNOWLEDGEMENTS

This research was funded by the Villum Kann Rasmussen (centre of Excellence NAMEC). The authors would like to acknowledge Michael Stenbæk Schmidt for his great discussion on this work. We also acknowledge the staffs at DTU Danchip for their efforts in microfabrication.

REFERENCE

[1] S.T. Koev, M.A. Powers, H. Yi, L.Q. Wu, W.E. Bentley, G.W. Rubloff, G.F. Payne, and R. Ghodssi, “Mechano-transduction of DNA hybridization and dopamine oxidation through electrodeposited chitosan network,” *Lab on a Chip*, vol. 7(1), pp. 103-111, (2007)

[2] M. Godin, V. Tabard-Cossa, Y. Miyahara, T. Monga, P. J. Williams, L. Y. Beaulieu, R. B. Lennox, and P. Grutter, "Cantilever-based sensing: the origin of surface stress and optimization strategies," *Nanotechnology*, vol.21, 075501, (2010).

[3] T. A. Brunt, E. D. Chabala, T. Rayment, S. J. Oshea, and M. E. Welland, "Measuring surface stress induced by electrode processes using a micromechanical sensor," *Journal of the Chemical Society-Faraday Transactions*, 92, pp.3807-3812, (1996)

[4] E. Seker, Y. Berdichevsky, M.R. Begley, M.L. Reed, K.J. Staley and M.L. Yarmush, “The fabrication of low-impedance nanoporous gold multiple-electrode arrays for neural electrophysiology studies,” *Nanotechnology*, vol. 21, 125504, (2010).

[5] D. Kramer, R. N.Viswanath, J. Weissmüller, “Surface-stress induced macroscopic bending of nanoporous gold cantilevers,” *Nano Lett.* 4, pp.793-796, (2004).

[6] G. G. Stoney, “The tension of metallic films deposited by electrolysis,” Proceedings of the Royal Society of London A-Materials, pp. 172–175, Jan. 1909.

[7] X. Quan, L.M. Fischer, A. Boisen, M. Tenje, “Development of nanoporous gold electrodes for electrochemical applications,” *Microelectronic Engineering*, vol. 88, pp.2379–2382, (2011).

[8] L. M. Fischer, C. Pedersen, K. Elkjær, N. N. Noeth, S. Dohn, A. Boisen, M. Tenje , “ Development of a microfabricated electrochemical-cantilever hybrid platform,” *Sensors and Actuators B*, vol.157, pp.321– 327, (2011).

[9] F. Weigend, F. Evers and J. Weissmller, “Structural relaxation in charged metal surfaces and cluster ions,” *Small,* vol. 2, no. 12, pp. 1497–1503, (2006).

[10] H. Pan, Y. Xu, S. Wu, B. Zhang and J Tang, “Molecular interactions in self-assembly monolayers on gold-coated microcantilever electrodes” *Nanotechnology*, vol. 22, 225503, (2011).

CONTACT

*Xueling Quan, tel: +45 45255890; Xueling.Quan@nanotech.dtu.dk