Fabrication And Characterization Of Surface-Modified Diamond Quartz Crystal Microbalance Electrode

Sachio Yoshihara*, Yanrong Zhang, Hiroaki Eguchi, Takashi Shirakashi
Department of Energy & Environmental Science, Graduate School of Engineering, Utsunomiya University
7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan

Introduction

Electrochemists are interested in diamond due to its unusual physical and chemical properties[1, 2]. However, by lacking of reliable *in situ* technique, the inherent underlying the phenomena is unclear.

Quartz crystal microbalance method has been widely used in electrochemical analysis as a powerful complementary technique. The fabrication of diamond - QCM will be anticipated to meet the need for diamond *in situ* researches. In this paper, a novel diamond sensor based on the QCM is described. This novel diamond-QCM sensor was fabricated by the reflow technique. The feasibility of the novel diamond-QCM sensor was evaluated by Raman spectroscopy, EPMA, electrochemical and simultaneous microgravimetric measurement, *etc*.

Experimental

1.Fabrication of diamond-QCM

Preparations of Boron-Doped Diamond(BDD) QCM substrate have been reported elsewhere[3)]. The diamond-QCM was regarded as as-grown diamond-QCM by the treatment described in the journal.

2. Apparatus and chemicals

Raman spectroscopy was obtained with a spectrometer using extended mode and Ar ion laser. The results of EPMA and XPS were obtained respectively. A potentiostat combined with a function generator was used for voltammetric measurement, the simultaneous electrochemical microgravimetry was performed with a plating Monitor, the CV and frequency responsive data were collected and analyzed by two computers, which connected with two sets up, respectively. Home-made diamond-QCM or commercial Au QCM was used as working electrode, a Pt mesh served as the counter electrode, a SCE electrode was used as reference and all potentials quoted in the following text were versus SCE. Analytical grade chemicals were used as purchased without further purification. Deionized water was used throughout the experiment.

The thickness of free-standing diamond film was measured by scanning electron microscopy (SEM) with a field emission-type instrument.

Results and discussion

1.Characterization of diamond films attached on QCM

Gold is soluble in Sn-Pb when the solder was heated to its melting point *ca*.1800C, whereas diamond is insoluble. After sputtered gold over its back, diamond film could be attached on the Sn-Pb preplated QCM by reflow without losing the oscillation of quartz crystal.

Raman microprobe spectroscopy is a tool that can provide high-revolution spatial information about diamond film microstructure, non-diamond carbon impurity phase, *etc*, and was used in this study. Figure shows the results of Raman spectroscopic study after diamond film attached over quartz crystal. One sharp and intensive peak due to sp3 carbon located at $1321 cm^{-1}$ was observed. The synthesized film is of the high quality and with significant diamond character, moderate boron-doped diamond[4)]. The result from Raman spectrum indicated that there is no significant crystallographic transition and contaminant induced during the procedure of diamond-QCM fabrication by the reflow technique.

2. Calibration of diamond-QCM

Iron electrodeposition from a 0.1M $Fe(NO_3)_2$ and 1M HNO_3 aqueous solution was performed to determine the correlation between the mass and the frequency of diamond-QCM in the study. The cathodic charge needed for iron deposition was obtained by integrated the area of current-potential curve in the potential range between –0.50V and –0.85V and deposited amount of iron was calculated from Faraday`s law. Here, the mass increasing per unit $1.41\times10^{-6} g/cm^2$ yields the shift of 68Hz in resonance frequency, the mass sensitivity of the diamond-QCM is:

$K=\Delta f/\Delta m$

Thus, for the diamond attached QCM, the mass sensitivity is –48.1 Hz $cm^2/\mu g$, whereas the theoretical value for a 4.67MHz crystal is –49.3 Hz $cm^2/\mu g$. The sensitivity of the diamond-QCM is about 2% lower than that of theoretical one.

3.Characterization of surface-modified diamond-QCM

Oxygen termination was performed by the anodic oxidation of as-grown diamond-QCM in 0.1M H_2SO_4, held the potential at +2.4V vs. SCE for 60min and was regarded as O-terminated diamond-QCM after the pretreatment.

Other surface modified BDD QCM"s were fabricated, *eg.* Cl-terminated, NH_2-terminated, L-Cystein-terminated BDD's. More detail comparison between each terminated BDD electrode will be discussed in my presentation.

Our final Goal of this research project is the fabrication of more sensitive digital-type DNA tip using moderately modified BBD electrode.

REFERENCES

1 P. W. May, *Endeavour Magazine*, 19(3), (1995) 101
2 B. V. Sarada, T. N. Rao, D. A. Tryk and A. Fujishima, *New Diamond Front. Carbon Technol.*, 9 (1999) 365.
3.
4. J. Wang, G. M. Swain, M. Mermoux, G. Lucazeau, J. Zak and J. W. Strojek, *New Diamond Front. Carbon Technol.*, 9 (1999) 317.

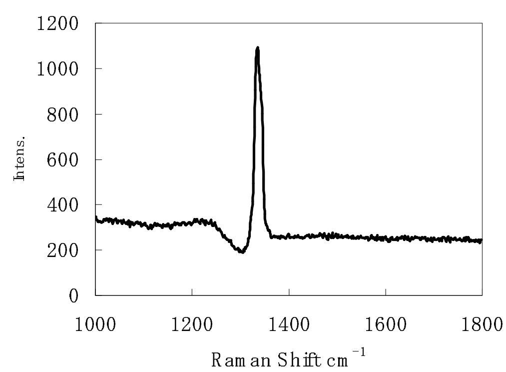

Figure Raman spectrum of boron-doped diamond