

Dual-Channel Quartz-Crystal Microbalance for Sensing Under UV Radiation

著者	安部 隆
journal or publication title	IEEE sensors journal
volume	7
page range	321-322
year	2007
URL	http://hdl.handle.net/10097/34673

Dual-Channel Quartz-Crystal Microbalance for Sensing Under UV Radiation

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Abstract—*In situ* measurements of interfacial phenomena with subatomic resolution under environmental disturbances have been a major goal of engineers and scientists engaged in the development of a microbalance sensor. Here, we demonstrate *in situ* measurements of the photooxidation process of alkanethiol self-assembled monolayers using dual-channel quartz-crystal microbalance (D-QCM) sensor that uses spherically contoured resonators to acoustically separate sensing channels for simultaneous compensation of environmental disturbances. Using a photolithographic method to make the D-QCM, the reference channel used in parallel with the sensing channel has almost the same resonant frequency and temperature coefficient of frequency. As a result, mass changes of 10-pg order accuracy were observed under ultraviolet radiation over four days.

Index Terms—Dual-channel, photooxidation, quartz crystal microbalance (D-QCM), SAM.

I. INTRODUCTION

GENERALLY, the sensor response is not associated with the quantity being measured because of environmental drift such as temperature. It is well known that photooxidation by UV exposure leads to temperature drift. Frequency errors due to this temperature drift limit the accuracy of the mass measurement. For example, an AT-cut resonator (9-MHz fundamental mode) shows at least a 1-ppm frequency shift for each 1 K of temperature change. This frequency error of 1 ppm equates to several molecular layers of water. Therefore, mass change can not be accurately determined without temperature control. To compensate for the environmental disturbance and provide sub-atomic-layer resolution, we have developed a dual-channel quartz crystal microbalance (D-QCM) using the photolithographic method [1]. The use of photolithography is very important because two sensors need to be fabricated spatially close in order to cancel environmental disturbances. For miniaturization, it is known that the reduction of unwanted spurious responses is of paramount importance to avoid vibration coupling. In order to reduce the generation of spurious modes and obtain a high quality resonator, we decided to fabricate a convex shaped QCM. Conventionally, the convex crystal resonator has been produced by polishing and has some problems, for example, difficulty in miniaturization and bulk fabrication and surface damage on the polished side. Combining the photolithographic and dry etch processes offers new

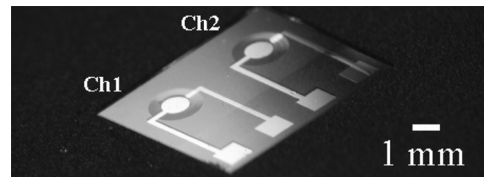


Fig. 1. Photograph of the D-QCM fabricated by the photolithographic method.

promising approaches to the manufacture of QCMs with high Q, small diameters, and monolithic integration on a substrate [1], [2].

In this work, *in situ* measurement of the photooxidation of alkanethiol was carried out by using the D-QCM. The photooxidation has been analyzed by Raman spectroscopy, SIMS and XPS. These analyses suggested that the photooxidation involved photooxidation of thiol to sulfonates and sulfur-carbon bond scission [3]. However, the photooxidation has not been *in situ* measured.

II. METHODS

The optical photograph of the D-QCM is shown in Fig. 1. The dimensions of fabricated QCMs are 1-mm-diameter electrodes and 2-mm-diameter convex formation. The thickness of the AT-cut quartz crystal, which has good temperature characteristic, is about 97 μm after the fabrication.

The resonator array having resonant frequencies (17 MHz) within the frequency difference of 50 ppm was selected for the use as the D-QCM. The optimum convex height was chosen to acoustically separate the resonator. When the convex depth is 1.6 μm , a quality value of about 80 000 is found for the bi-convex type resonator. In this study, all resonators used for the D-QCM were etched at least 3% of total thickness.

The mass resolution of the fabricated sensor was evaluated by electroplating nickel on the electrode. The mass was checked by the thickness and the density. The mass resolution was estimated at 11 ± 1 pg/Hz. This is close to the theoretically predicted value of 12 pg/Hz.

The temperature coefficient of the resonant frequencies was measured, and the frequency shifts because of a temperature change were within 4 ppm between 300 and 333 K. The difference of the frequency between resonators is within 1 Hz.

III. RESULTS AND DISCUSSION

The fabricated D-QCM showed only a 2-Hz frequency change during 24 h of monitoring, without any environmental control. The changes were not dependent on time, remaining within several Hertz over four days. The frequency response to variations in intensity of UV light are shown in Fig. 2. Here, the reference channel is channel 1 (Ch1) and the sensing channel is channel 2 (Ch2). UV light from a high-pressure mercury lamp (HAMAMATSU, LC5) was radiated uniformly. The frequency

Manuscript received October 4, 2006; accepted October 11, 2006. This work was supported in part by the Ministry of Education, Culture, Sports, Science, and Technology of Japan, Grant-in-Aid for Young Scientists (A) No.18681017 and in part by PRESTO of Japan Science and Technology Corporation (JST). The associate editor coordinating the review of this paper and approving it for publication was Prof. Fabien Josse.

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Digital Object Identifier 10.1109/JSEN.2006.890165

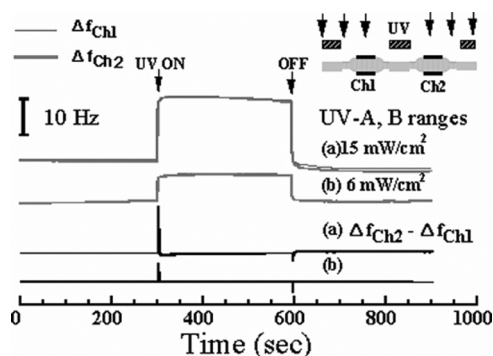


Fig. 2. Examples of frequency responses for UV radiation.

responses were almost the same, the difference was negligible. For example, the difference in resonant frequency between Ch1 and Ch2 was about 0.2 Hz for 6 mW/cm^2 and about 0.6 Hz for 15 mW/cm^2 . The intensity shown here is measured in the UV-A and B ranges. The corresponding intensities at 254 nm are 0.18 and 0.45 mW/cm^2 , respectively. The positive shift in resonant frequency due to the radiation is explained by the absorption of UV light. The resulting frequency response versus radiation intensity of UV light in the UV-A and B ranges exhibits a linear relationship.

The photooxidation of a self-assembled monolayer was measured to show the usefulness of the D-QCM. The sensing electrode was dipped into an 0.01-mM ethanolic solution of decanethiol (Mw. 174.3) for 10 min. Then, the sample was sonicated in ethanol for 1 min to remove any unbound thiols on the Au electrode. The frequency shift because of the binding is about 140 Hz. This value is close to the adsorption amount reported (1.3 nmol/cm^2) and the corresponding frequency change (160 Hz). We dried the samples in vacuum and then exposed them to UV light. The UV intensity was held constant at 20 mW/cm^2 over the UV-A and B ranges (0.6 mW/cm^2 at 254 nm). The key point of our experiment is that the high-pressure mercury lamp is employed for monitoring the slow photooxidation of alkanethiol. Fig. 3 shows the frequency responses with exposure of UV light on the monolayer. To show the utility of the D-QCM, the frequency response measured by a single QCM (S-QCM) is shown in Fig. 3(a). This shows that the frequency drift depends on the environment. Under the exposure of strong UV light, *in situ* measurement is impossible by using the S-QCM. On the other hand, the frequency shift measured by the D-QCM detects an interesting phenomenon

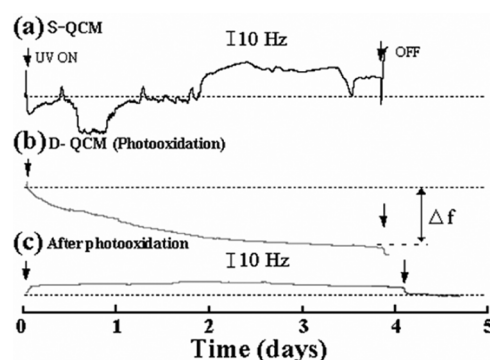


Fig. 3. *In situ* measurement of the photooxidation of alkanethiol self-assembled monolayer by using D-QCM.

as shown in Fig. 3(b). The frequency decreased gradually over time. This change is explained by oxidization of thiol groups. It is well known that UV (254 nm) radiation breaks the Au-S bond and oxidizes the sulfur atom forming SO_3 [3]. The high-pressure lamp used in this work emits very weak intensity of light with a wavelength of 254 nm. Thus, the photooxidation was completed after four-days-irradiation of UV light. Without any films on Au, no change was measured when the lamp was turned off. The frequency change (c.a. 44 Hz) corresponds to the mass of three oxygen (39 Hz). The difference is explained by adsorption of water. To check the reproducibility, we tried the measurement repeatedly. Fig. 3(c) shows the frequency shift with UV exposure measured again after the photooxidation was completed. The frequency gradually increased when the lamp was turned on. After the lamp was turned off, the frequency decreased with the total frequency change within 2 Hz (equal to 20 pg). Here, the temperature at the resonator is raised up to about 333 K and the frequency change was not observed when the both of electrodes are coated by thiols. Thus, it is reasonable to explain the frequency shift by water desorption and adsorption on the photooxidized monolayer.

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