Development of an Active Oxygen Detector Using a Quartz Crystal Microbalance with a Carbon/Silver Layer

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We have developed a new method for detecting active oxygen using a carbon/silver-coated quartz crystal microbalance. Active oxygen is detected by monitoring the increase in frequency due to decreased carbon mass resulting from the reaction with active oxygen. Detection of atomic oxygen radical generated in an oxygen plasma device was verified for practical future application. The results show that this method allows precise measurement of atomic oxygen and accurate detection of the carbon layer's disappearance from the frequency behavior.

In recent years, with increasing demand for the reduction of greenhouse gas emissions (e.g., fluorocarbons used in semiconductor processes) into the atmosphere, the use of active oxygen has been attracting attention. Active oxygen generated by methods such as ultraviolet lamps,[1] ozonizers, and discharge plasma is a key factor in various industrial processes such as surface cleaning, surface modification, sterilization, and oxidization. Accurate measurement of active oxygen is critical for control of these processes. However, this measurement requires costly specialized equipment incorporating a laser optical system or a vacuum ultraviolet light source, and there is a need for a feasible method that readily enables the real-time measurement of active oxygen.

We investigated the use of the quartz crystal microbalance (QCM) technique for the detection of active oxygen. The QCM is a sensor device that allows nanogram-order measurement of changes in mass on a quartz crystal surface by observing frequency shifts.[2]

Figure 1 shows a schematic diagram of the QCM with a carbon/silver layer. In this study, a commercially available AT-cut quartz crystal (SC-101, Maxtek, Inc.) was prepared as a QCM oscillator with a resonant frequency of 6 MHz. The active-oxygen detection layer consisted of a silver layer and a carbon layer, sequentially coated on a gold electrode by vacuum deposition. The surface roughness (*R*a: the arithmetic average of the absolute values of roughness) of the quartz crystal, which greatly affects the sensing sensitivity, was confirmed by AFM to be approximately 12.2 nm.

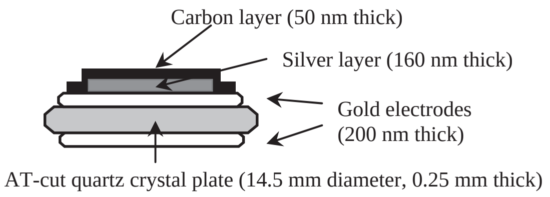

Figure 1. Schematic of the QCM with a carbon/silver layer.

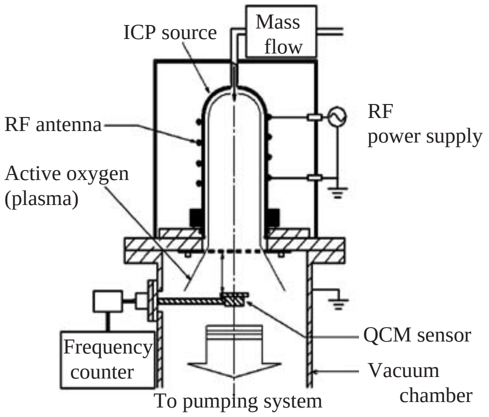

Figure 2. Experimental setup.

Figure 2 shows the experimental setup. The equipment features an inductively coupled plasma (ICP) source in the upper part of the vacuum chamber. The vacuum chamber was evacuated to less than 0.1 Pa using a rotary pumping system, then oxygen gas (5N purity) was introduced at a flow rate of 0.025, 0.033, 0.045, or 0.05 standard liters/min (SLM) at a pressure of 13, 16, 19, or 23 Pa, respectively. After the pressure was stabilized, RF (13.56 MHz) power at 200 W was fed to the antenna through the matching network and inductively coupled oxygen plasma was generated inside the ICP source. Although many active oxygen species (e.g., oxygen ion, excited molecular state, ozone, etc.) are assumed to exist in such plasma, we have confirmed by a spectroscopic study that atomic oxygen radical is the predominant active oxygen generated in this apparatus.[3] These atomic oxygen radicals are assumed to flow downward owing to the evacuation and then to be detected by the QCM.[4] The QCM sensor was inserted in the sensor head and connected to the oscillation circuit at a position 35 mm below the ICP source and on the central axis of the equipment. Frequency shifts during plasma generation were monitored every 30 s for 25 min by a frequency counter (SC-7205, Iwatsu), and the results were recorded.

Our previous study verified the feasibility of measuring active oxygen by a QCM with either a silver monolayer or a carbon monolayer.[5] It was found that in the silver-layer QCM, the frequency showed rapid changes without linearity owing to drastic surface oxidation by atomic oxygen radicals (Figure 3).[6] Moreover, this type of QCM did not allow stable and long-term detection of active oxygen because of poor reproducibility and reliability due to wide variations of the silver layers.

On the other hand, the carbon-layer QCM showed stable detection characteristics. However, there are some cases in which frequency peaking, i.e., carbon disappearance resulting from the

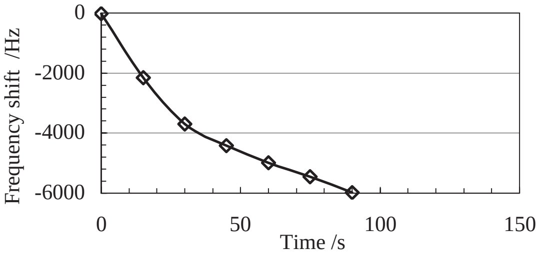

Figure 3. Typical frequency shift of a QCM with a silver monolayer (resonant frequency: 9 MHz, electrode diameter: 5 mm, RF power: 100 W, oxygen gas flow rate: 0.02 SLM).

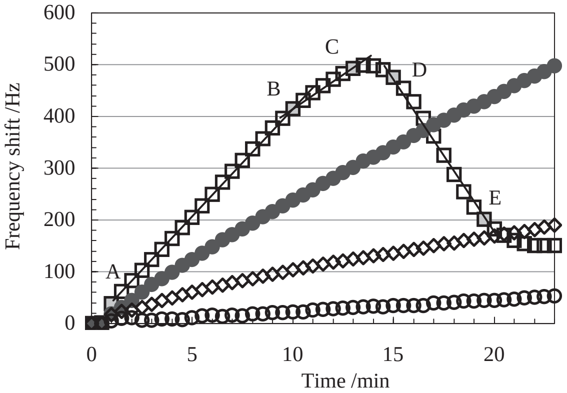

Figure 4. Frequency shift of the carbon/silver QCM. □ at 13 Pa, ● at 16 Pa, ◇ at 19 Pa, and ○ at 23 Pa.

reaction with active oxygen, cannot be clearly detected because of frequency drift, which causes difficulties in practical use. To solve these problems, we have developed a new QCM sensor with a carbon/silver layer that takes advantage of the characteristics of silver and carbon and studied its application to the detection of atomic oxygen.

Figure 4 shows the frequency shift of the carbon/silver-coated QCM during irradiation with atomic oxygen at several oxygen pressures. At a pressure of 13 Pa, the frequency increased linearly up to 415 Hz over a period of 10 min at a constant rate of 41.5 Hz/min (slope A–B). This indicates that the carbon layer reacted with atomic oxygen radicals, gradually losing mass through the formation of volatile flux (e.g., CO and CO_2). Subsequently, the frequency increase rate changed to ca. 27.2 Hz/min (slope B–C) and shifted from an increase to a decrease between 13 and 14.5 min (C–D). It is assumed that carbon reduction led to a partial exposure of silver and that the exposed silver layer gained mass from reacting with atomic oxygen, forming silver oxide (Ag_2O, etc.). We confirmed the disappearance of carbon on the surface of an irradiated specimen by elemental analysis using energy dispersive spectroscopy (EDS).

Furthermore, the frequency continued to decrease (D–E), apparently because silver oxidation exceeded carbon reduction after the inflection point. These results suggest that silver oxidation can be utilized for active oxygen detection even after the carbon layer has disappeared and that practical application of a QCM with a carbon/silver layer is feasible.

The rate of atomic oxygen flux affecting the sensor surface is estimated by the frequency increase (slope A–B) and by the following equation:[7]

$$O^*flux = \Delta m \cdot R/(M_c \cdot S \cdot t) \qquad (1)$$

where Δm is the change in mass of the carbon, R is Avogadro's number (6.022×10^{23}/mol), M_c is the mass of removed carbon (12 g/mol), S is the area of carbon layer irradiated by atomic oxygen (approx. 0.5 cm^2), and t is the measurement time (600 s). Note that the frequency shift of 1 Hz corresponds to a mass change of approx. 19 ng at the QCM with a resonant frequency of 6 MHz. From eq 1, an atomic oxygen flux of 1.21×10^{15} atoms/cm^2/s was obtained.

In the same manner as above, atomic oxygen fluxes of 7.50×10^{14}, 3.28×10^{14}, and 6.93×10^{13} atoms/cm^2/s at 16, 19, and 23 Pa were obtained. We also confirmed a drastic decrease of the emission intensity of atomic oxygen (777 nm) with increasing oxygen pressure, which corresponds to these calculated values.

The possible time for detection of active oxygen can also be determined by observing the inflection point. In other words, the frequency drift that has been a problem with the conventional carbon monolayer QCM can be suppressed, and application of this QCM to industrial processes is considered to be feasible. This experiment showed that the actual time for detection of active oxygen by the carbon layer was ca. 10 min (A–B). We believe that this duration is sufficient for accurate estimation of the atomic oxygen flux.

In conclusion, we have designed a new method for measuring active oxygen utilizing a QCM. This method enables not only accurate measurement of active oxygen, which affects various processes but also identification of the disappearance of the carbon detection layer. We, therefore, believe that this method has significant advantages in practical application compared with the conventional monolayer type QCM. In this study, atomic oxygen generated under an inductively coupled oxygen plasma environment was monitored using a QCM with a carbon/silver layer. The result obtained showed an oxygen flux of ca. 1.2×10^{15} atoms/cm^2/s at 13 Pa. These devices with a simple structure can be manufactured at low cost and are suitable for mass production, and, therefore, have great potential for use as monitors enabling the selectable detection of active oxygen species in industrial processes.

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