

Investigation of Silver Oxidation Behavior under Active Oxygen Processing Utilizing the Quartz Crystal Microbalance Method

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We have been investigating the mechanism of surface oxidation on thin silver film under ultraviolet lamp processing to achieve high-resolution active oxygen monitoring utilizing a quartz crystal microbalance (QCM). In this study, real-time silver oxidation behavior was measured by the QCM. The oxidation mechanism is discussed here based on the results of surface analyses by X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM).

The use of ultraviolet (UV) lamps has become widely established in various industrial applications over the past several decades.¹ In particular, the surface sterilization of pathogens under UV lamps has been attracting a great deal of public attention against the background of the global prevalence of contagious viruses. Multiple methods of sterilization are advocated involving not only UV radiation but other techniques as well, with atomic oxygen considered to be one of the most effective of these.² However, a practical method for the quantification of atomic oxygen with an easy-to-use sensing monitor device has not yet been realized. We have been investigating the quartz crystal microbalance (QCM) method as a candidate for the solution of this issue. Of special note is a QCM with a silver detection layer (hereafter referred to as "silver-QCM"), which has high sensitivity to atomic oxygen³ and can be employed even in environments with a small amount of active oxygen because the sensor can detect nanogram-order mass changes on the electrode as the frequency changes. However, atomic oxygen detection utilizing the silver-QCM has the serious drawback that the sensing values become saturated during measurement owing to deterioration of the silver surface.⁴ It is, therefore, important to analyze the phenomenon of silver oxidation on the QCM in order to precisely quantify its effect on the atomic oxygen value. In this study, we investigated the oxidation mechanism of the silver detection layer under a UV light source to gain a fundamental understanding of the detection capability of the QCM.

In the present study, we used a low-pressure mercury UV lamp (QGL90U-31, Iwasaki Electric) as an active oxygen source. It is known that ozone (O₃) and excited atomic oxygen (O¹D) are generated under UV radiation (185/254 nm) via photochemical reactions, with atomic oxygen being the predominant oxidant in the process.⁵ A silver-coated quartz crystal (SC-101, Maxtek Inc.) with a resonant frequency of 6 MHz was used as an atomic oxygen sensor. The sensor consisted of a thin silver film with a thickness of ca. 200 nm, a chrome adhesion layer of ca. 20 nm in thickness, and a quartz substrate, set in a sensor head.

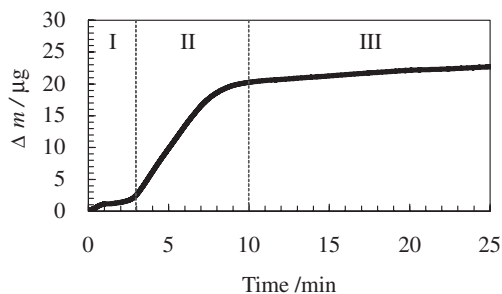


Figure 1. Typical mass change of silver-QCM.

The detection area of the sensor was 8 mm in diameter. The distance between the UV lamp and the sensor head was set at 10 mm. Both the UV lamp and the QCM sensor were located in the lamp box. The experimental atmosphere was ambient air with exhausting of generated ozone, as in practical use. The sensor was connected to an oscillator (Q-pod, Sigma Instruments), and the frequency shift while the lamp was turned on was recorded. To prevent thermal drift of the QCM, the sensor head temperature was maintained at a constant 20 °C by circulating water.

Figure 1 shows the typical mass change characteristics of the silver-QCM. The data was mean value of three experiments. Note that the measured frequency-shift value was converted to mass change using the value of 16 ng per 1 Hz at 6 MHz quartz. The mass slightly increased up to an elapsed time of 3 min. It is thought that ozone and/or atomic oxygen was adsorbed to the silver surface in this duration (region I). After 3 min, the mass steeply increased (region II) and then exhibited a gentle rise (region III). These results suggest that the silver surface was abruptly oxidized by atomic oxygen and formed a silver oxide layer, after which naked silver existing under the formed silver oxide layer was gradually oxidized.

To clarify these hypotheses, we performed various analyses on the silver surfaces exposed to atomic oxygen. First, we analyzed the oxidized silver surfaces by in-plane X-ray diffraction (XRD) (Ultima-IV, Rigaku). The details of this method are described in ref 6. Figure 2 shows typical in-plane XRD patterns obtained for incident angles of 0.2 and 0.5° on surfaces irradiated with UV for 1 min (Figure 2a) and 10 min (Figure 2b).

The results reveal that the silver oxide structure was not detected on the surface irradiated with UV for 1 min by this method. It is interesting to note that Ag₂O was the only type of silver oxide formed, rather than Ag₂O₂ (AgO). As reported by Gao

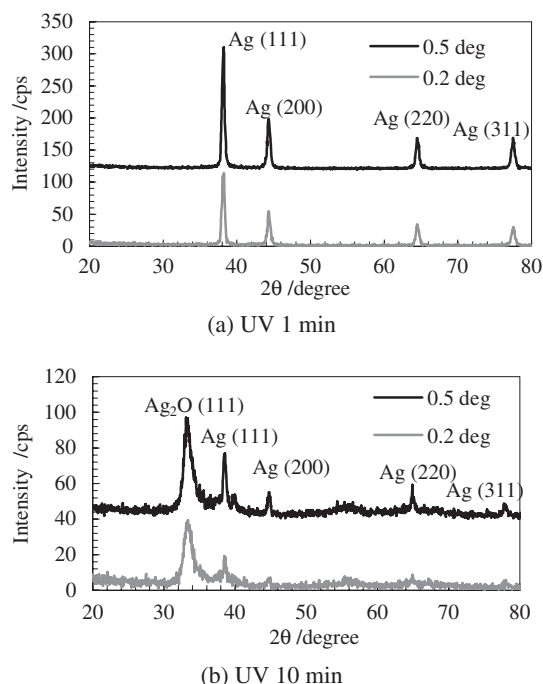


Figure 2. In-plane XRD patterns of silver-QCM.

et al. in their experiments on Ag_2O film deposition with ion-beam sputtering, formed Ag_2O structure is less stable than Ag_2O and easily decomposed.⁷ This indicates that atomic oxygen reacts only with the naked silver, so that further oxidation does not occur. For the X-ray incident angle of 0.2° in the case of UV irradiation for 10 min, strong $\text{Ag}_2\text{O}(111)$ and weak $\text{Ag}(111)$ orientation are seen. In contrast, the X-ray incident angle of 0.5° shows Ag_2O and various Ag peaks. This result indicates that most of the surface was fully oxidized by atomic oxygen, whereas the interior was not yet oxidized. In the case of 0.5° , the X-ray penetration depth is believed to be a few atomic layers or more. However, it is difficult to give a clear definition of the depth because the determination is strongly affected by the surface state (e.g., surface roughness).

We, therefore, prepared a thinned specimen using ion milling and analyzed its cross-sectional structure by scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectrometry (EDXS) (Tecnai F20, FEI Corporation). The analysis results are shown in Figure 3. It was found that oxygen existed on the surface region at a depth of only a few tens of nanometers or less in the specimen irradiated with UV for 1 min (Figure 3a). From the chemical shift of the Auger peak (Ag MNN, 902.2 eV) exhibited in analysis by X-ray photoelectron spectroscopy (XPS) (Axis-Ultra, Cratos), the oxidized silver layer was confirmed to have an Ag_2O structure. We believe that the reason why the silver oxide layer was not detected by XRD is that the layer has an amorphous and/or microcrystalline structure, on the basis of the fact that both XRD and XPS are able to detect information on the surface region only to a depth of a few nanometers.

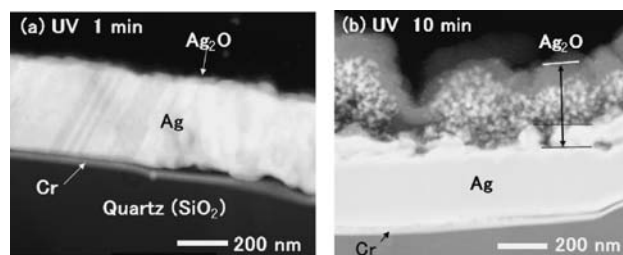


Figure 3. Cross-sectional STEM images of silver-QCM.

In the case of the specimen irradiated for 10 min, on the other hand, the thickness of the oxidized silver layer was up to ca. 300 nm, comprising an upper weak boundary layer and a lower relatively dense layer (Figure 3b). The tendency of these results is roughly consistent with the estimated thickness by silver-QCM measurements (Figure 1).

From these results, the mechanism of oxidation on the silver detection layer is considered to be as follows: First, the silver surface strongly reacts with atomic oxygen, and structural distortion is then generated on the surface with increasing Ag_2O thickness. By top-view observation with a scanning electron microscope (JSM-6300F, JEOL), we confirmed the existence of structural distortion due to volume expansion resulting from the formation of a thick Ag_2O layer. Subsequently, atomic oxygen diffuses into the inner layer through the distortion and reacts with the naked silver. Oxidation gradually progresses through the repetition of this process. Since the UV light (185/254 nm), to which the QCM is constantly exposed during measurement, has sufficient energy to activate the silver surface (>4.8 eV), this might also assist the formation of the Ag_2O layer.

In conclusion, we have investigated silver oxidation using a QCM. From our analyses, the details of silver oxidation behavior were clarified. As a result, the effective detection time using a silver-QCM is considered to be within a few minutes under our experimental conditions.

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References

- 1 J. R. Vig, *Proc.-Electrochem. Soc.* **1990**, 190, 105.
- 2 O. Kylian, T. Sasaki, F. Rossi, *Eur. Phys. J. Appl. Phys.* **2006**, 34, 139.
- 3 V. Matijasevic, E. L. Garwin, R. H. Hammond, *Rev. Sci. Instrum.* **1990**, 61, 1747.
- 4 F. Imai, K. Kunimori, H. Nozoye, *J. Vac. Sci. Technol. A* **1995**, 13, 2508.
- 5 H. Okabe, *Photochemistry of Small Molecules*, Wiley-Interscience, New York, **1987**, pp. 177–183.
- 6 S. Takahashi, M. Taniguchi, K. Omote, N. Wakabayashi, R. Tanaka, A. Yamagishi, *Chem. Phys. Lett.* **2002**, 352, 213.
- 7 X. Gao, S. Wang, J. Li, Y. Zheng, R. Zhang, P. Zhou, Y. Yang, L. Chen, *Thin Solid Films* **2004**, 455–456, 438.