Reaction Monitoring of Gold Oxides Prepared by an Oxygen-dc Glow Discharge from Gold Films in Various Aqueous Solutions by a Surface Plasmon Resonance-based Optical Waveguide Sensing System and X-ray Photoelectron Spectroscopy

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Abstract

The chemical properties of thin (~0.6 nm) gold oxide layers prepared by an oxygen-dc glow discharge from gold films at room temperature in various solvents and solutions were studied using a surface plasmon resonance (SPR)-based optical waveguide sensing system and X-ray photoelectron spectroscopy (XPS). New insights into the stability and reactivity of gold oxides under these conditions were obtained. The O 1s XPS spectra show three oxygen species, comprising components I, II, and III, in the gold oxides and components I and II are present in this order from the top surface of the oxide (component III). The gold oxide is stable in various solvents (water, methanol, ethanol, acetone, acetonitrile, diethyl ether, chloroform, hydrocarbons) for 10–30 min at room temperature. The gold oxide decomposes in aqueous $10^{-2}$ M solutions of acetaldehyde, hydrochloric acid, and sodium hydroxide during these periods. Gold oxide decomposition in these solutions was monitored by SPR and the decomposition rates were obtained. Decomposition of the gold oxides was confirmed and their surfaces were characterized after decomposition by XPS.

(172 words)

Keywords Gold oxide, oxygen-dc glow discharge, reaction property, aqueous solution, acetaldehyde, hydrochloric acid, sodium hydroxide, decomposition rate, SPR, XPS
Introduction

A hydrophobic gold film surface can be changed into a hydrophilic surface by forming a gold oxide layer on it. However, the gold oxide decomposes back into gold over time or after heating because of its instability.\textsuperscript{1} Gold oxides have previously been prepared by oxidation of gold in highly reactive chemical environments, such as reactive sputtering in an oxygen atmosphere,\textsuperscript{2,3} ozone,\textsuperscript{4-7} and oxygen plasma.\textsuperscript{8-13} These oxides have also been prepared using an air corona discharge\textsuperscript{14} and via laser deposition in oxygen.\textsuperscript{15} The gold oxides that occurred on the gold electrodes of microelectromechanical system (MEMS) devices after the release of organic sacrificial layers caused by exposure to oxygen plasma were also characterized.\textsuperscript{16-19} It has previously been reported that the gold oxides on the gold electrodes of MEMS devices can be removed effectively via treatment with aqueous hydrochloric acid\textsuperscript{16,17} or heating.\textsuperscript{18,19} Plasma surface treatments using various gases, including oxygen, for bonding with thin gold films and with stub bumps were also compared.\textsuperscript{20,21} Gold oxides that were present on gold nanoparticles were also investigated and the results were reported previously.\textsuperscript{22-26} Since little is known about the chemical properties of gold oxides, it is important to understand them for future applications.

X-ray photoelectron spectroscopy (XPS)\textsuperscript{27,28} is a useful method for characterization of thin gold oxide layers on gold films. The gold oxides, which were prepared via various methods, all decomposed immediately at higher temperatures,\textsuperscript{2,5,7-9,11,13,18,19,21} while they decomposed relatively slowly at room temperature.\textsuperscript{9,12} The gold oxides were also found to contain oxygen species other than the gold oxides and these species remained stable at higher temperatures. These oxygen species were assigned to be hydroxyl groups;\textsuperscript{2-4,8,9,12,15,20} however, the evidence for this remains unclear and some discrepancies exist. Theoretical studies of the adsorption and dissociation of water molecules on both gold surfaces and oxygen-covered gold surfaces were performed.\textsuperscript{29,30} The results showed that the dehydrogenation reaction of the water molecules on
the oxygen-covered gold surfaces was favorable and that the gold surface was covered with hydroxyl groups.

Gold oxide layers with thicknesses of less than 1 nm were prepared by an oxygen-dc glow discharge over various periods (0.5–10 min) from gold films at room temperature and were characterized by XPS in our previous papers.31,32 A schematic representation of the formation and decomposition of a gold oxide layer with a thickness of approximately 0.6 nm prepared by an oxygen-dc glow discharge (10 Pa, 5 mA, 10 min) from a gold film is shown in Fig. 1. The O 1s XPS spectra showed three oxygen species comprising components I, II, and III in the gold oxides, as shown in Table 1. Components I and II have both been assigned to hydroxyl groups and are stable up to 500°C, but differ only in the vertical position.31,32 The angular dependence of the XPS spectra of the gold oxides indicated that the oxygen species of components I and II are present in this order from the top surface of the gold oxide (component III).

The gold oxides decomposed after 36 h at room temperature and decomposed immediately at temperatures exceeding 121°C in a dark atmosphere. These gold oxides also decomposed under ultraviolet (UV) light irradiation (254, 302, and 365 nm) at room temperature and decomposed more rapidly in water vapor at the shorter wavelengths. These findings suggested that the gold oxide decomposition is accelerated via a reaction with excited water molecules produced by UV light absorption. The gold oxide decomposed after 6 h in water but decomposed more slowly in hydrocarbons (hexane, octane, and dodecane) at room temperature in a dark atmosphere. The gold oxide can be preserved in the oxidized state for 84 d in anhydrous dodecane.32 This simple method for preservation of a gold oxide immersed in a hydrocarbon with low water content will be helpful for practical use in future applications. Since a hydrophobic gold film surface can be changed into a hydrophilic surface by forming a gold oxide layer on it, the gold oxide layer formation by an oxygen-dc glow discharge from a gold film is promising as a new hydrophilization technology for the gold surface. Information about the stability and reactivity of gold oxides in solvents and
solutions is important in addition to methods for preservation of the oxides.

In this work, the following studies were conducted to understand the chemical properties of this unique metal oxide. The stability of thin (approximately 0.6 nm) gold oxide layers prepared from gold films by an oxygen-dc glow discharge in various solvents was studied at room temperature using a surface plasmon resonance (SPR)-based optical waveguide sensing system and XPS. The decomposition reactions of these thin gold oxide layers on gold films in aqueous solutions of acetaldehyde, hydrochloric acid, and sodium hydroxide were monitored and their decomposition rates were obtained via the SPR-based optical waveguide sensing system for the first time. The decomposition of each of the gold oxides was confirmed and the oxide surfaces after decomposition were characterized by XPS.

Experimental

Gold oxide preparation

The gold oxide layers on 50-nm-thick gold films were prepared by vacuum deposition of gold (>99.99%, Tanaka Kikinzoku Kogyo, Tokyo, Japan) on cleaved mica substrates (dimensions: 9 mm × 18 mm × 0.1 mm; Nisshin EM, Tokyo, Japan) followed by an oxygen-dc glow discharge at room temperature under high vacuum (<6.7×10⁻⁴ Pa) conditions. A calibrated thickness monitor (XTM/2, Leybold Inficon, East Syracuse, NY, USA) was used to measure both the deposition rate and the gold film thickness. An oxygen-dc glow discharge (10 Pa, 5 mA, 10 min) from a high-purity oxygen (>99.999%, Japan Fine Products, Kawasaki, Japan) flow in a vacuum evaporator that was equipped with a negatively-biased (to approximately 400 V) aluminum electrode was then used to oxidize the gold films. Impurities that originated from neither the gold used (e.g., Ag, Cu, Ca, Si) nor the glow discharge (e.g., Al, Fe, F) were detected on the gold oxide surfaces by XPS. Carbon impurities that incorporated oxygen atoms from the
air were detected on the surfaces and their effects on the O 1s spectra of the gold oxides prepared by the oxygen-dc glow discharge (10 min) were estimated to be less than 2%.

**SPR measurements**

The SPR spectra of the solvents and the aqueous solutions used for the gold oxide layers on the gold films in the 380–1000 nm wavelength range were measured using an optical waveguide sensing system equipped with a xenon lamp with a filter (System Instruments SIS-5000, Hachioji, Tokyo, Japan). The wavelength resolution was 1.25 nm. Gold oxide layers on gold films (50 nm thick and 2 mm × 5 mm) that were deposited directly on a waveguide ($n_d = 1.80610$; Sumita Optical Glass, Saitama, Japan) were used. Both the angle of incidence and the output angle were 29º and the light was reflected once at the bottom of the 2-mm-wide gold film. The SPR spectra of 100 µl of each of the solvents (H$_2$O, CH$_3$OH, and C$_2$H$_5$OH) and the aqueous solutions (CH$_3$CHO, HCl, and NaOH) in a liquid cell made from a silicone rubber sheet were measured at room temperature with a cover over the waveguide to prevent evaporation. The SPR spectrum of water was measured first using the gold film; a gold oxide layer was then formed and the SPR spectra of the solutions were measured. These SPR spectra were measured on the gold oxide layers every 1 or 0.5 min for 10–30 min. The peak wavelength at the minimum in the response curve was obtained from a fitting process with the second order curve in the ±20 nm range because the error from the least squares method is smaller. The decomposition rates of the gold oxide layers in the aqueous solutions were calculated by differentiating the peak wavelengths with respect to time at three points. The refractivities of the solvents and the aqueous solutions were measured at 25°C using an Abbe refractometer (RX-5000α-Bev; Atago, Tokyo, Japan) and the measurement uncertainties were less than 1×10$^{-4}$ refractive index (RI) units.
**XPS measurements**

The XPS spectra of the gold oxide layers on the gold films were measured after they were immersed in various solvents (H$_2$O, CH$_3$OH, C$_2$H$_5$OH, (CH$_3$)$_2$C=O, CH$_3$CN, (C$_2$H$_5$)$_2$O, and CHCl$_3$) for 15 min at room temperature. The spectra of the gold oxides were also measured after being immersed in 10$^{-4}$–10$^{-2}$ M aqueous solutions (CH$_3$CHO, HCl, and NaOH) for 15 or 30 min and 10$^{-2}$ M aqueous solutions (HNO$_3$ and H$_2$SO$_4$) for 15 min at room temperature and then rinsed using water.

A photoelectron spectrometer (Axis-Ultra DLD, Shimadzu, Kyoto, Japan) with monochromatic Al K$_\alpha$ (1486.6 eV) radiation was used to measure the XPS spectra of the gold oxide layers on the gold films. These XPS spectra were measured within 1 h after completion of each sample. The measurement resolution was estimated to be less than 0.6 eV from the peak width of the Ag 3d$_{3/2}$ line at 368.3 eV. The spectra were measured at angle of 90° from the surfaces (dimensions: 0.7 mm × 0.3 mm) at data collection intervals of 0.1 eV. The deconvolution of the Au 4f and O 1s peaks was performed using the Voigt function after subtraction of the Shirley background. The intensity ratio of the Au 4f$_{7/2}$ and Au 4f$_{5/2}$ peaks was 4/3. The Au 4f$_{7/2}$ line at 84.0 eV was used to calibrate the binding energy. Because the calibration level for the binding energy was less than 0.1 eV, the low-energy electron flood gun that is applied for sample charge compensation was not used in this case. The gold oxide decomposition during the measurement period (approximately 6 min) under X-ray irradiation in the spectrometer was estimated to be less than 1% by measuring the same sample twice. The relative intensities of both pairs of oxide peaks with respect to the metal peaks of Au 4f were used to calculate the thicknesses of the gold oxide layers on the gold films. The photoelectron inelastic mean free paths of 1.781 and 1.937 nm in Au and Au$_2$O$_3$ and the atomic densities of 19.32 and 13.675 g/cm$^3$ for Au and Au$_2$O$_3$ were used, respectively. The atomic ratio [O]/[Au] of the gold oxide (Au$_2$O$_3$) was calculated from the intensities of oxide component III of O 1s and those of the Au 4f oxide peaks.
using the XPS spectrometer’s software. The results of characterization of the gold oxide layers prepared from gold films by an oxygen-dc glow discharge (10 Pa, 5 mA, 5 and 10 min) at room temperature are presented in Table 2. A second photoelectron spectrometer (ESCA-1000, Shimadzu, Kyoto, Japan) was used to perform the preliminary measurements.

Results and Discussion

Reaction properties of gold oxides in solvents

The typical SPR spectra of water measured from a gold film and from a gold oxide layer (0.65 nm) on the gold film at room temperature (19.2°C) (upper) and their peak wavelengths during a 15 min period (lower) are shown in Fig. 2. The penetration depth of the evanescent wave into the sample caused by SPR is several hundred nanometers. Therefore, the entire gold oxide layer exists within the wavelength range and is detected by SPR. The average values and the standard deviations of the peak wavelengths of both spectra are also shown in the figure. The peak wavelength of the SPR spectrum of water when measured from the gold oxide layer on the gold film shifts toward longer wavelengths of 11.8 nm when compared with that measured from the gold film and the wavelength remained constant during this period. The SPR spectrum of water measured from the gold oxide layer on the gold film shows that the gold oxide remains stable in the water for this period. Therefore, water is a suitable medium for monitoring of the reactions of the gold oxide in various aqueous solutions.

The SPR spectra of methanol and ethanol were also measured from the gold oxide layers on the gold films at room temperature (17.1–29.8°C) for 15 min and their average peak wavelengths are given along with those of water in Table 3. The peak wavelengths of the SPR spectra of these alcohols also remained constant during this period and shifted toward longer wavelengths as their refractivities increased. The gold oxides remained stable in these alcohols.
and these solvents are thus also suitable for monitoring the reactions of gold oxides in these solutions.

The XPS spectra of Au 4f and O 1s for gold oxide layers on gold films when immersed in water, methanol, and ethanol for 15 min at room temperature (13.9–16.6°C) are shown in Fig. 3. The corresponding spectra for a gold oxide that was not subjected to immersion and was measured within 1 h after preparation of the oxide is also shown for comparison purposes. The Au 4f spectra show the 4f$_{7/2}$ and 4f$_{5/2}$ pair of strong metal peaks at 84.0 and 87.7 eV and a pair of oxide peaks at the higher binding energies of 85.8 and 89.4 eV. The O 1s spectra show three oxygen species comprising components I, II, and III in the gold oxides at 532.0, 531.0, and 529.8 eV, respectively. The relative intensities of the oxide Au 4f peaks and the oxide component III in the gold oxides differ slightly for each immersion, as illustrated in Table 4, but the gold oxides are preserved after immersion in these solvents. The XPS spectra of Au 4f and O 1s from the gold oxide layers on the gold films when immersed in acetone, acetonitrile, diethyl ether, and chloroform also showed no decomposition in the gold oxides. Gold oxides can also be preserved for long periods in hydrocarbons (hexane, octane, and dodecane). The results above indicate that gold oxide remains stable in these solvents and that these solvents are thus suitable for studying the oxide reactivity in the solutions.

**Reaction properties of gold oxides in aqueous acetaldehyde solutions**

The peak wavelengths of two SPR spectra of an aqueous acetaldehyde solution of $1.7 \times 10^{-2}$ M when measured from gold oxide layers on gold films during a 15 min period at room temperature (29.8°C) (upper) and the differentials of the peak wavelengths (the reaction rates) of the oxides (lower) are shown in Fig. 4. The peak wavelengths of both the SPR spectra of water that were measured from the corresponding gold films are also shown for comparison purposes. The two peak wavelengths measured from the gold oxide layers on gold films are different.
because the SPR measurement conditions are not necessarily the same each time, but the changes in the peak wavelength over time agree well. The peak wavelength decreased with time and reached a constant value after 9 min, indicating a reduction in the thickness of the gold oxide layer in the solution. The peak wavelength of the SPR spectrum after 9 min is longer than that for the corresponding gold film. This finding indicates the presence of residual species on the surface. The refractivity of the solution was 1.3326 at 25°C and there was no change from the water within the measurement uncertainty range. The reaction rates of both gold oxide layers agree well with each other and it is thus possible to monitor the reaction of the gold oxide in this solution.

The XPS spectra of Au 4f and O 1s from the gold oxide layers on the gold films when immersed in $1.7 \times 10^{-4}$, $1.7 \times 10^{-3}$, and $1.7 \times 10^{-2}$ M aqueous acetaldehyde solutions for 15 min at room temperature (25.4°C) are shown in Fig. 5. The relative intensities of the oxide Au 4f peaks in the spectra obtained from the $1.7 \times 10^{-4}$ M solutions agreed well with that measured from the sample without immersion, as shown in Table 5. This indicates that no reaction occurred in the gold oxide in this solution. The relative intensities of the oxide Au 4f peaks in the spectra that were obtained from the $1.7 \times 10^{-3}$ M solutions were smaller than those obtained from the $1.7 \times 10^{-4}$ M solutions. The spectra of Au 4f and O 1s that were obtained from the $1.7 \times 10^{-2}$ M solution showed neither the oxide Au 4f peaks nor the O 1s component III. The XPS spectra of Au 4f and O 1s for the gold oxide layer that were obtained from the $1.7 \times 10^{-2}$ M solution show complete decomposition of the oxide on the gold film, and this finding is consistent with the results obtained from SPR measurements. The O 1s spectrum shows the peak of component I of the hydroxyl groups on the gold surface. This peak corresponds to the residual species that were observed in the SPR spectrum after 9 min. The gold oxide layer (0.65 nm) was found to decompose via a reduction reaction in a $1.7 \times 10^{-2}$ M aqueous acetaldehyde solution and it decomposed completely after 9 min at room temperature. Decomposition of gold oxides was also observed in $1.2 \times 10^{-3}$ and $1.2 \times 10^{-2}$ M formaldehyde solutions using XPS.
Reaction properties of gold oxides in aqueous hydrochloric acid solutions

The peak wavelengths of the two SPR spectra of a 1.2×10^{-2} M aqueous hydrochloric acid solution when measured from gold oxide layers on gold films over 10 min at room temperature (19.6 and 29.5°C) (upper) and the differentials of the peak wavelengths (the reaction rates) of the oxides (lower) are shown in Fig. 6. The peak wavelengths of both SPR spectra of water when measured from the corresponding gold films are also shown for comparison purposes. The two peak wavelengths that were measured from the gold oxide layers on the gold film were slightly different, but the changes in the peak wavelengths over time agreed well. The peak wavelength decreased with time and reached a constant value after approximately 7 min. The peak wavelength of the SPR spectrum after 7 min is longer than that from the corresponding gold film. This finding indicates the presence of residual species on the film surface. The refractivities of the solution was 1.3326 at 25°C and there was no change from the water within the measurement uncertainty range. The reaction rates of the two gold oxide layers agree well and it is thus possible to monitor the reaction of gold oxide in this solution.

The XPS spectra of Au 4f and O 1s from the gold oxide layers on the gold films when immersed in 1.2×10^{-4}, 1.2×10^{-3}, and 1.2×10^{-2} M aqueous hydrochloric acid solutions for 15 min at room temperature (23.8°C) are shown in Fig. 7. The relative intensities of the oxide Au 4f peaks in the spectra obtained from the 1.2×10^{-4} M solution agreed well with the results obtained from the sample without immersion, as shown in Table 5. This indicates that no reaction with the gold oxide occurred in this solution. The relative intensities of the oxide Au 4f peaks in the spectra that were obtained from the 1.2×10^{-3} M solution become smaller than those obtained from the 1.2×10^{-4} M solution. The XPS spectra of Au 4f and O 1s from the gold oxide layer that were obtained from the 1.2×10^{-2} M solution showed complete decomposition of the oxide on the gold film, and this finding is consistent with the results that were obtained from the SPR measurements. The O 1s spectrum shows the peak of component I from the hydroxyl groups on the gold surface.
This peak corresponds to the residual species that were observed in the SPR spectrum after 7 min. The gold oxide layer (0.65 nm thick) was found to decompose in a $1.2 \times 10^{-2}$ M aqueous hydrochloric acid solution and decomposed completely after 7 min at room temperature. However, the gold oxide layers on gold films do not decompose when immersed in aqueous solutions of both nitric acid ($1.3 \times 10^{-2}$ M) and sulfuric acid ($1.2 \times 10^{-2}$ M) for 15 min at room temperature (19.1°C), as illustrated by the XPS spectra of Au 4f and O 1s shown in Fig. 8. It was found that the gold oxides do not decompose in these acid solutions at the same concentration as that of the hydrochloric acid solution. Therefore, it is believed that a water-soluble tetrachloroauric acid ($\text{H[AuCl}_4\text{]}$) $^{34-36}$ is produced by the reaction of the gold oxide and the hydrochloric acid in the solution. Decomposition of gold oxides was also observed in $1.1 \times 10^{-3}$ and $1.1 \times 10^{-2}$ M hydrobromic acid solutions using XPS.

Reaction properties of gold oxides in aqueous sodium hydroxide solutions

The peak wavelengths of the two SPR spectra of an aqueous sodium hydroxide solution of $1.0 \times 10^{-2}$ M when measured from gold oxide layers on gold films during a 30 min period at room temperature (18.6 and 27.9°C) (upper) and the differentials of the peak wavelengths (the reaction rates) of the oxides (lower) are shown in Fig. 9. The peak wavelengths of both SPR spectra of water when measured from the corresponding gold films are also shown for comparison purposes. Both the peak wavelengths and the peak shift values measured from the gold oxide layers on the gold film are different. The peak shift value that was measured from the gold oxide layer at 18.6°C was the larger of the two. However, the changes in the peak wavelength over time agreed well. The peak wavelength decreased over time and reached a constant value after approximately 22 min. The peak wavelength of the SPR spectrum after 22 min is longer than that in the corresponding gold film. This finding indicates the presence of residual species on the gold film surface. The solution refractivity was 1.3327 at 25°C and there was almost no change from that
of water within the measurement uncertainty range. The reaction rates of the two gold oxide layers agree well and it is thus possible to monitor the reaction of the gold oxide in this solution.

The XPS spectra of Au 4f and O 1s from the gold oxide layers on the gold films when immersed in 1.0×10⁻⁴, 1.0×10⁻³, and 1.0×10⁻² M aqueous sodium hydroxide solutions of for 30 min at room temperature (24.7°C) are shown in Fig. 10. The relative intensities of the oxide Au 4f peaks in the spectra that were obtained from the 1.0×10⁻⁴ M solution agree well with those measured from the sample without immersion, as shown in Table 5. This indicates that no reaction with the gold oxide occurred in this solution. The relative intensities of the oxide Au 4f peaks in the spectra that were obtained from the 1.0×10⁻³ M solution become slightly smaller than those obtained from the 1.7×10⁻⁴ M solution. The XPS spectra of Au 4f and O 1s from the gold oxide layer obtained from the 1.0×10⁻² M solution show complete decomposition of the oxide on the gold film; this finding is consistent with the results obtained from the SPR measurements. The O 1s spectrum mainly shows the peak of component I of the hydroxyl groups on the gold surface. This peak corresponds to the residual species that were observed in the SPR spectrum after 22 min. The gold oxide layer (0.65 nm thick) was found to decompose in a 1.0×10⁻² M aqueous sodium hydroxide solution and it decomposed completely after 22 min at room temperature. Decomposition of gold oxides was also observed in 1.0×10⁻³ and 1.0×10⁻² M potassium hydroxide solutions using XPS. Gold hydroxide (Au(OH)₃) nanoparticles were prepared from an aqueous solution of tetrachloroauric acid (H[AuCl₄]) by raising the solution pH and the precipitate structure was characterized by electron microscopy, Mössbauer spectroscopy, X-ray analysis, and thermal analysis.³⁶ The water solubility of Au(OH)₃ at room temperature was reported to be 1.20 mg/100 g of H₂O. The Au L₃-edge X-ray absorption spectrum of a [Au(OH)₃]⁻ solution was also shown. It is believed that the gold hydroxide (Au(OH)₃) is produced by the reaction of the gold oxide with the sodium hydroxide, and that it is dissolved in the solution from these results. The formation of [Au(OH)₃]⁻ is also considered.
Conclusions

The reaction properties of gold oxide layers with thicknesses of approximately 0.6 nm that were prepared by an oxygen-dec glow discharge from gold films were studied using an SPR-based optical waveguide sensing system and XPS. The gold oxide remains stable in various solvents (water, methanol, ethanol, acetone, acetonitrile, diethyl ether, chloroform, and hydrocarbons) for 10–30 min at room temperature, which means that these solvents are suitable for study of the oxide reaction properties. The gold oxide decomposes in aqueous $10^{-2}$ M solutions of acetaldehyde, hydrochloric acid, and sodium hydroxide during the same periods. The decomposition of each of the gold oxides in these aqueous solutions was monitored by SPR and the oxide decomposition rates were obtained for the first time. The decomposition characteristics of the gold oxides were confirmed and their surfaces were also characterized using XPS. The residual species that are present after the decomposition are the hydroxyl groups on the gold surfaces. The information obtained about the chemical properties of the gold oxides will be important in enabling the future use of this unique oxide as a new hydrophilization technology for hydrophobic gold surfaces.

Acknowledgements

The preliminary study was conducted by Mr. T. Ohata and Mr. T. Okuno. The authors thank Dr. H. Takahashi of System Instruments Co., Ltd. for his support with the SPR optical waveguide sensing system. The authors also thank Mr. S. Kubo in the Division of Instrumental Analysis, Research Support Center, Kagoshima University for his support of the XPS measurements. Funding: This research was supported by the Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP) from the Japan Science and Technology Agency.
(JST) [grant number VP30218088452]; and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology [grant number 26410156]. We thank David MacDonald, MSc, from Edanz Group (www.edanzediting.com/ac) for editing a draft of this manuscript.

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Figure Captions

**Fig. 1** Schematic representation of formation and decomposition of a gold oxide layer with thickness of approximately 0.6 nm prepared from a gold film by an oxygen-dc glow discharge (10 Pa, 5 mA, 10 min). Images of water droplets dropped on a gold film and on a gold oxide layer are also shown. A hydrophobic gold film surface is changed to a hydrophilic surface by formation of a gold oxide layer. Oxygen species of components I and II are assigned to hydroxyl groups and are present in this order from the top surface of the gold oxide (component III). The gold oxide is decomposed by heating or UV light irradiation and thus provides the hydroxyl groups (components I and II) on the gold film.

**Fig. 2** Typical SPR spectra of water when measured from a gold film and from a gold oxide layer on the gold film at room temperature (19.2°C) (upper) and their peak wavelengths during a 15 min period (lower). The peak wavelength of the SPR spectrum of water measured from the gold oxide layer on the gold film (●) shifts to wavelengths of about 12 nm longer than that measured from the gold film (○) and the wavelength remained constant during this period.

**Fig. 3** XPS spectra of Au 4f and O 1s for gold oxide layers on gold films when immersed in water, methanol, and ethanol for 15 min at room temperature (13.9–16.6°C). The corresponding XPS spectra of a gold oxide layer that was preserved for the same period in a dark atmosphere are also shown. The Au 4f spectra show a pair of oxide peaks and the O 1s spectra have three components. These spectra show that gold oxides remain stable in these solvents over this period.

**Fig. 4** Peak wavelengths of two SPR spectra of a 1.7×10^{-2} M aqueous acetaldehyde solution measured from gold oxide layers on gold films at room temperature (29.8°C) during a 15 min
period (upper) and differentials of the peak wavelengths (decomposition rates) of the oxides (lower) (■ and ●). The peak wavelengths of two SPR spectra of water that were measured from the corresponding gold films are also shown (□ and ○).

**Fig. 5** XPS spectra of Au 4f and O 1s for gold oxide layers on gold films when immersed in aqueous acetaldehyde solutions of various concentrations (1.7×10^{-4}, 1.7×10^{-3}, and 1.7×10^{-2} M) for 15 min at room temperature (25.4°C). The gold oxide decomposes in the 1.7×10^{-2} M solution after 15 min and this provides the oxygen species (component I) on the gold film.

**Fig. 6** Peak wavelengths of two SPR spectra of a 1.2×10^{-2} M aqueous hydrochloric acid solution measured from gold oxide layers on gold films at room temperature (upper) and differentials of the peak wavelengths (decomposition rates) of the oxides (lower) (■: 19.6°C and ●: 29.5°C). The peak wavelengths of two SPR spectra of water that were measured from the corresponding gold films are also shown (□ and ○).

**Fig. 7** XPS spectra of Au 4f and O 1s for gold oxide layers on gold films when immersed in aqueous hydrochloric acid solutions of various concentrations (1.2×10^{-4}, 1.2×10^{-3}, and 1.2×10^{-2} M) for 15 min at room temperature (23.8°C). The gold oxide decomposes after 15 min in the 1.2×10^{-2} M solution and this provides the oxygen species (component I) on the gold film.

**Fig. 8** XPS spectra of Au 4f and O 1s for gold oxide layers on gold films when immersed in aqueous nitric acid and sulfuric acid solutions with concentrations of 1.3×10^{-2} and 1.2×10^{-2} M, respectively, for 15 min at room temperature (19.1°C). The XPS spectra of the gold oxide when immersed in water for the same period are also shown. The gold oxides remain stable in the acid solutions for this period.
Fig. 9  Peak wavelengths of two SPR spectra of a $1.0 \times 10^{-2}$ M aqueous sodium hydroxide solution measured from gold oxide layers on gold films at room temperature (upper) and differentials of the peak wavelengths (decomposition rates) of the oxides (lower) (■: 18.6°C and ●: 27.9°C). The peak wavelengths of two SPR spectra of water that were measured from the corresponding gold films are also shown (□ and ○).

Fig. 10  XPS spectra of Au 4f and O 1s for gold oxide layers on gold films when immersed in aqueous sodium hydroxide solutions of various concentrations ($1.0 \times 10^{-4}$, $1.0 \times 10^{-3}$, and $1.0 \times 10^{-2}$ M) for 30 min at room temperature (24.7°C). The gold oxide decomposes after 30 min in the $1.0 \times 10^{-2}$ M solution and this provides the oxygen species (mainly component I species) on the gold film.
Table 1  Peak energies (PE) of Au 4f and O 1s and full width at half maximum (FWHM) values obtained from XPS of gold oxide layers prepared from gold films by an oxygen-dc glow discharge (10 Pa, 5 mA, 10 min) at room temperature

|             | PE (eV) | FWHM (eV) | O 1s    | PE (eV) | FWHM (eV) |
|-------------|---------|-----------|---------|---------|-----------|
| Au 4f       |         |           |         |         |           |
| 4f$_{7/2}$ (metal) | 84.0    | 0.8       | Component I (hydroxyl group) | 532.0 | 1.9 |
| 4f$_{7/2}$ (oxide)  | 85.8    | 1.6       | Component II (hydroxyl group) | 531.0 | 1.8 |
| 4f$_{5/2}$ (metal) | 87.7    | 0.8       | Component III (oxide) | 529.8 | 1.7 |
| 4f$_{5/2}$ (oxide)  | 89.4    | 1.6       |         |         |           |

Uncertainties are less than ±0.1 eV.

Table 2  Characterization results of gold oxide layers prepared from gold films by an oxygen-dc glow discharge (10 Pa, 5 mA) at room temperature

| Discharge time (min) | Gold oxide thickness (nm) | Atomic ratio [O]/[Au] | Ratios of O 1s components I | II | III |
|----------------------|---------------------------|-----------------------|-----------------------------|----|-----|
| 5                    | 0.62±0.06                 | 1.67±0.18             | 0.08±0.02                   | 0.45±0.03 | 0.47±0.05 |
| 10                   | 0.65±0.11                 | 1.78±0.18             | 0.17±0.09                   | 0.46±0.05 | 0.38±0.06 |

The number of data for the discharge times of 5 and 10 min are 14 and 12, respectively, and the uncertainties are standard deviations.

Table 3  Average peak wavelengths for 15 min and corresponding shift values in the SPR spectra of methanol, water, and ethanol measured at 17.1–29.8°C from gold oxide layers (0.65±0.11 nm thick) prepared from gold films (approximately 50 nm thick) by an oxygen-dc glow discharge (10 Pa, 5 mA, 10 min)

|                      | Methanol | Water    | Ethanol    |
|----------------------|----------|----------|------------|
| Refractivity (RI units, 25°C) | 1.3270   | 1.3325   | 1.3594     |
| Peak wavelength (nm)  | 563.1±2.3 (32) | 576.9±3.2 (23) | 587.5±2.4 (32) |
| Peak shift (nm)       | 0        | 13.8     | 24.4       |

The number of data is shown in parentheses in each case. The uncertainties are standard deviations.
Table 4  Ratios of peak intensities of oxide Au 4f and O 1s (component III) in XPS spectra of gold oxide layers (0.65±0.11 nm thick) after immersion in methanol, water, and ethanol for 15 min at 13.9–27.5°C compared with those measured within 1 h after preparation (without immersion)

|       | No immersion (12) | Methanol (2) | Water (17) | Ethanol (2) |
|-------|-------------------|--------------|------------|-------------|
| Au 4f | 0.31±0.06         | 0.34±0.03    | 0.30±0.03  | 0.41±0.03   |
| O 1s (III) | 0.38±0.06   | 0.39±0.05    | 0.36±0.06  | 0.43±0.03   |

The number of data is shown in parentheses in each case. The uncertainties for the no immersion case and for water are standard deviations and those for methanol and ethanol are differences between the two values.

Table 5  Ratios of peak intensities of oxide Au 4f and O 1s (component III) in XPS spectra of gold oxide layers (0.65±0.11 nm thick) after immersion in aqueous solutions of acetaldehyde ($f$=1.7, 15 min, 14.0 and 25.4°C), hydrochloric acid ($f$=1.2, 15 min, 14.1 and 23.8°C), and sodium hydroxide ($f$=1.0, 30 min, 12.8, 24.7, and 26.6°C)

|       | Acetaldehyde (2)          | Hydrochloric acid (2)          | Sodium hydroxide (4)          |
|-------|----------------------------|--------------------------------|-------------------------------|
|       | 10$^{-4}$ M, 10$^{-3}$ M  | 10$^{-4}$ M, 10$^{-3}$ M       | 10$^{-4}$ M, 10$^{-3}$ M      |
| Au 4f | 0.25±0.07 0.13±0.04       | 0.27±0.02 0.12±0.09            | 0.28±0.08 0.23±0.07           |
| O 1s (III) | 0.36±0.08 0.34±0.06       | 0.35±0.09 0.37±0.03            | 0.31±0.02 0.39±0.06           |

The number of data is shown in parentheses in each case. The uncertainties for acetaldehyde and hydrochloric acid are the differences between the two values and those for sodium hydroxide are standard deviations.
Graphical Abstract

Oxygen-dc glow discharge

\[ \text{Au}_2\text{O}_3 \]

Decomposition in solutions

\[ \text{Au} \]

Mica substrates

Al discharge ring

Gold deposition

H\(_2\)O

Intensity (%) vs. Wavelength (nm)

520 540 560 580 600 620
Oxygen-dc glow discharge

Component I
Component II
Component III

Thermal / UV decomposition

Component I
Component II
Fig. 2. M. Higo et al.
Fig. 3. M. Higo et al.
Fig. 4. M. Higo et al.
Fig. 5. M. Higo et al.
Fig. 6. M. Higo et al.
Fig. 7. M. Higo et al.
Fig. 8. M. Higo et al.
Fig. 9. M. Higo et al.
Fig. 10. M. Higo et al.