Film-Thickness-Controllable System for Preparing Silver Nanofilms through Absorbance Monitoring of the Thickness during a Silver-Mirror Reaction

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An innovative technique is proposed for forming silver thin films of nanometer-order thickness *via* a silver-mirror reaction. This approach is made possible by the real-time monitoring of the thickness of a silver thin film formed on the edge surface of a fiber core during the silver-mirror reaction using a homemade absorbance measurement system. The monitored absorbance value increases as silver plating progresses, and the relationship between the absorbance values and the thickness of the silver thin film is linear in the thickness range from approximately 30 to 60 nm. This technique was applied to the preparation of a fiber-optic surface plasmon resonance (FO-SPR) sensor. The sensor was successfully used to measure sucrose solutions with concentrations of less than 16% (w/v). The sensitivity of the sensor probe was estimated to be 2205 nm/RIU in the refractive index range of 1.333 – 1.357. The relative standard deviation of the wavelength shift obtained from measurements using different sensor probes was estimated to be less than 3.3%.

Keywords Surface plasmon resonance, silver-mirror reaction, optical fiber, electroless plating, sensor

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Introduction

Thin metal films with nanometric-order thickness have distinct advantages over bulk materials,^{1–3} and the technique used to deposit such films is considered to be the key to designing new materials based on their properties. Physical methods of vacuum evaporation and sputtering are commonly used to deposit thin metal films and provide the greatest level of control of their thickness, thereby resulting in the highest-quality films.⁴ These methods require large and expensive dedicated instruments and facilities. However, with advances in electroless plating techniques, the deposition of metal thin films with nanometer-scale thickness has become feasible. Electroless plating is an attractive deposition technique because the deposition of metal thin films is carried out by immersing the target object in plating bath solutions with a nonthermal external energy source.^{5–7} However, the poor reproducibility of the thickness of the thin films creates difficulties when using electroless plating to fabricate new materials in the form of metal thin films.

Although various methods for measuring the nanometer-order thickness of metal thin films have been developed, including spectroscopic ellipsometry,^{8,9} X-ray fluorescence spectrometry,^{10,11} atomic force microscopy (AFM)^{12,13} and scanning electron microscopy (SEM),¹⁴ few methods are capable of monitoring

the film thickness in real time. A quartz crystal microbalance (QCM) is commonly used for the real-time monitoring of film thickness in physical metal deposition methods. Thickness measurements by QCM, which must be positioned near to the target object, rely on tracking of the frequency response of a quartz crystal during the deposition process; this indirect monitoring plays an important role in controlling the thickness of a deposited thin metal. However, using QCM to monitor the thickness of a deposited metal film during electroless plating is difficult because of the difference in the deposition rates between the target object and the quartz crystal. This difference stems from differences in the amounts of ion catalysts adsorbed onto the surface of target objects and the quartz crystal.

Some researchers investigated changes in optical properties of nanometer-order-thick metal thin films,^{15–17} and we focused on the investigation to establish an approach to the real-time monitoring of their thickness. This method is based on real-time measurements of the transmittance of a metal thin film during the deposition process. The results suggested that this method is applicable to various deposition methods, including physical metal deposition methods and electroless plating. The approach may be particularly well suited to electroless plating because the thickness of the metal thin film on the target object can be monitored directly, potentially enabling control of the thickness of the film.

In the present study, an optical fiber was used as the target object model and we developed a real-time monitoring system based on the transmittance of a metal thin film on an optical

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Fig. 1 A absorbance measurement system for real-time monitoring of the thickness of a silver thin film formed during the silver-mirror reaction.

fiber tip during the silver-mirror reaction. We used the system to monitor the deposition of silver and possibly control its thickness. The technique was used to fabricate a fiber-optic surface plasmon resonance (FO-SPR) sensor,^{18–22} which has attractive advantages, including remote sensing,^{18,19} easy operation, and the miniaturization of whole systems, compared with prism-based SPR sensors.^{20–22}

Experimental

Materials

All reagents used in the present study were of analytical reagent grade unless otherwise specified. Milli-Q water (Millipore Reagent Water System, Bedford, MA, USA) was used in all of the experiments. Dilute nitric acid, sulfuric acid, ethanol, potassium hydroxide, glucose and sodium chloride were obtained from Kanto Chemical Co. (Tokyo, Japan). Hydrogen peroxide, a silver nitrate solution, an ammonia solution, saccharin, tin(II) chloride dihydrate and hydrochloric acid were purchased from Fujifilm Wako Pure Chemical (Tokyo, Japan). The silver powder was obtained from Nilaco (Tokyo, Japan). Tollens' reagent used for the silver-mirror reaction was prepared using a silver nitrate solution, an ammonia solution and potassium hydroxide. The silver plating solution was prepared by diluting solution 4 times with a 137 ppm saccharin solution.

Principle of silver thin-film formation by real-time monitoring of absorbance

Figure 1 shows the absorbance measurement system used for the real-time monitoring of the thickness of the silver thin film. This system comprises a power LED (OSW4XNE3C1E, OptoSupply, HK, China), a homemade power supply for the power LED, a Teflon beaker, a fiber adapter (BFA-KIT, Ocean Insight, FL, USA), a fiber-optic cable (M28L01, Thorlabs, NJ,

USA) and a spectrometer (USB4000, USB4E03214, Ocean Insight, FL, USA). The power LED, a multimode fiber with an exposed core, a fiber adapter, and the light-receiving part of the fiber-optic cable were arranged in a straight line. The incident light emitted from the power LED was irradiated to the edge surface of the fiber core, and the transmitted light emitted from an opposite edge surface of the fiber was detected with a spectrometer *via* a fiber-optic cable. The transmitted light intensity at 458 nm was obtained in the interval of 1 s. The transmittance (I_t/I_0) was calculated by the ratio of the transmitted light intensity at the start of the silver-mirror reaction (I_0) and that at time t (I_t). In addition, the transmittance was converted to absorbance with the software "OceanView" (version 1.5.2, Ocean Insight, FL, USA). An increase in the thickness of silver thin film by the silver-mirror reaction resulted in a decrease in the transmittance, *i.e.* the increase in absorbance. The absorbance data obtained for the silver-mirror reaction using the fiber tip was recorded using a notebook PC.

Pretreatment of optical fiber

An optical fiber with a core diameter of 400 μm (FT400UMT, Thorlabs, NJ, USA) was cut to a length of 100 mm, and both end surfaces of the fiber were smoothly polished with a fiber polishing machine (Radian TrigLT™, KRELLTECH, NJ, USA). To expose the core surface of the fiber, the fiber jacket and cladding with a length of 3 mm were removed from one end of the fiber using a fiber stripping tool (T21S31, Thorlabs, NJ, USA) and acetone cotton, respectively. The core surface was cleaned by immersion in a piranha solution prepared by combining hydrogen peroxide and sulfuric acid of a volume ratio of 1:3, and ultrapure water (in this order).

Fabrication of a silver thin film on the optical fiber core while monitoring for thickness

The Tollens' reagent was diluted fourfold with water and saccharin was added to the diluted reagent to a concentration of

137 ppm (referred to hereafter as the reaction solution). A 1.1 mL portion of the reaction solution was poured into a microtube, which was then placed in the developed system (Fig. 1). The fiber core was immersed in a 0.2 w/v% SnCl_2 solution as a sensitizer (prepared with 0.01 M hydrochloric acid) at 30°C for 5 min and then into the reaction solution cooled to -2°C by ice water containing sodium chloride. The silver-mirror reaction was started by adding a 405 μL of 10 mM glucose solution as a reducing reagent to the reaction solution, *i.e.*, saccharin concentration reached 100 ppm, and a silver thin film was gradually formed on the core surface of the fiber (Fig. S1, Supporting Information). When an arbitrary absorbance value of the silver thin film was reached, the optical fiber was immediately removed from the reaction solution using the Z-axis stage. The surface of the silver thin film on the fiber core was thoroughly washed by immersion in ultrapure water, and the fiber was stored in a plastic case until immediately before use. In the case of preparing an optical-fiber SPR sensor, the optical fiber was removed from the reaction solution when the absorbance value reached 1.25.

Evaluation of the sensor probe by measuring sucrose solutions

The performance of the fabricated SPR sensor probe was evaluated using a homemade FO-SPR sensor (Fig. S2, Supporting Information). This sensor was composed of a fabricated sensor probe (*i.e.* a silver-coated optical fiber removed from the reaction solution when the absorbance value reached 1.25), a halogen light source (KBEX-151B, Nissei Electric, Shizuoka, Japan), a bifurcated fiber and the spectrometer. The light emitted from the light source entered the sensor probe through one side of the bifurcated fiber. The incident light reflected on the inner surface of the silver film and was detected by the spectrometer. The wavelength of the SPR dip was calculated by normalizing the reflected light intensity (*i.e.* the ratio between the reflected light intensity obtained by the sensor probe in the sample solution and the sensor probe exposed to air). The performance of the sensor probe was evaluated by measuring sucrose solutions with various concentrations less than 16% (w/v).

Results and Discussion

Investigation of optimal conditions for the silver-mirror reaction

To deposit metal thin films with a smooth surface, we optimized certain experimental conditions, including the temperature of the silver-mirror reaction and the concentration of saccharin, which is an addition agent known to reduce the grain size.²³ After the reaction solution was prepared, the fiber core was coated with silver *via* the silver-mirror reaction at different temperatures. AFM measurements showed that the silver-mirror reaction at -2°C enabled the deposition of a silver film with a smooth surface (Fig. S3, Supporting Information). In the silver-mirror reaction, silver is coated onto the target object as particles and a high plating rate leads to the formation of large clusters.²⁴ A silver film with a smooth surface can be obtained at lower temperatures, *i.e.* lower plating rates.

In the approach for monitoring the film thickness based on the transmittance, the background originating from the optical absorption of the bath solution, *i.e.* the Tollens' reagent, interferes with monitoring of the transmittance. The progress of the silver-mirror reaction causes a color change to yellow, resulting in a background in the signal used to monitor the thickness. To prevent the color change, we optimized the saccharin concentration in the Tollens' reagent using a

Fig. 2 relationship between the absorbance of the reaction solution and the concentration of saccharin after the silver-mirror reaction was conducted for 10 min.

homemade monitoring system (Fig. 1). An optical fiber without a SnCl_2 treatment was drawn into the fourfold-diluted Tollens' reagent. The turbidity of the reagent at 10 min after the addition of a glucose solution was measured at 458 nm with a UV-vis spectrophotometer (Fig. 2). In the absence of saccharin, a higher turbidity was measured, whereas the turbidity decreased with increasing saccharin concentration. No turbidity was observed when the saccharin concentration reached 100 ppm, *i.e.* the optimum concentration. In subsequent experiments, silver thin films were formed under the optimized condition.

Real-time monitoring of thickness of the silver thin film on the fiber core during the silver-mirror reaction

The approach to thickness monitoring based on transmittance change was demonstrated with a homemade transmitted-light-intensity measurement system (Fig. 1). During coating of the fiber core with the silver thin-film *via* the silver-mirror reaction, the time course of the transmitted light intensity was monitored over the wavelength range from 400 to 850 nm. The transmitted light intensity decreased with increasing reaction time (Fig. 3(a)). Photographs from before and after plating are shown in Fig. 3(b). These indicate that the growth of the silver thin film resulted in a decrease in the transmitted light intensity. In particular, the transmitted light intensity at wavelengths of 458 and 525 nm greatly decreased compared with that before plating. However, the transmitted light intensity at 525 nm might be influenced by the SPR signal generated by the formation of a silver thin film. Therefore, the wavelength to be monitored was determined to be 458 nm. Figure 3(c) shows the absorbance at 458 nm, estimated from the time course of the change in transmitted light intensity. The increase in the absorbance with time was observed when the optical fiber treated with SnCl_2 as a sensitizer was used. Such an increase in absorbance was not observed when the untreated fiber was used. The low reaction temperature, *i.e.*, -2°C , and the presence of saccharin induced a decrease in the rate of the silver mirror reaction, leading to silver deposition onto only the SnCl_2 treated fibers, *i.e.*, silver was not deposited onto the wall surface of the microtube and the fibers untreated with SnCl_2 .

Fig. 3 (a) Change in the transmitted light spectra for the silver-mirror reaction as a function of time. (b) Optical fiber with a silver thin film formed on the fiber core before and after the silver-mirror reaction. (c) Time course of absorbance at 458 nm during the silver-mirror reaction, as monitored with fibers with and without a silver thin film. The measurement without a silver thin film was carried out using an optical fiber not treated with SnCl₂ solution.

Relationship between the silver film thickness and absorbance value

To estimate the thickness of the silver thin films on the basis of their measured absorbance, we investigated the relationship between the thickness and the absorbance. Silver thin films with a thickness from 20 to 50 nm were formed on cover glasses using a vacuum evaporation apparatus (E-120, ALS Technology, Kanagawa, Japan) equipped with a deposition port filled with silver powder. The absorbance of the films was measured with a UV-Vis spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). We also evaluated the thickness of the films by AFM.

After a small part of the silver thin film was removed using a dilute nitric acid solution to expose the surface of the cover glass, the distance between the surface of the silver thin film and the exposed surface of the cover glass was measured (Fig. 4(a)). A plot of the absorbance as a function of the film thickness showed a linear relationship ($y = (0.0320 \pm 0.0031)x - 0.4046 \pm 0.1345$, $R^2 = 0.972$) in the thickness range from 25 to 65 nm. This relationship indicates that the absorbance of the silver thin films can be used to estimate their thickness.

The thickness of silver thin films on fiber cores was estimated using our developed transmittance measurement system. In the case of the fibers, a higher thickness of the silver thin film induced higher absorbance values (Fig. 4(b)), as similar to the case of cover glasses. The absorbance values recorded during the silver-mirror reaction were proportional to the film thickness obtained from AFM measurements ($y = (0.0311 \pm 0.0021)x - 0.3004 \pm 0.0935$) (Fig. 4(c)). The linearity was $R^2 = 0.945$, as determined by comparisons with silver thin films deposited onto cover glasses by vacuum evaporation. Therefore, in our approach, the thickness of silver thin films could be monitored in real time during the silver-mirror reaction when using the equation obtained in Fig. 4(c).

Observation of SPR signal

The real-time monitoring of the thickness of silver thin films was demonstrated, and its application to preparing an FO-SPR sensor probe was investigated. The FO-SPR sensor probe requires a 40–60 nm-thick silver thin film on the core surface.²⁴ In our approach, an absorbance of 1.25 corresponds to a 50 nm-thick silver thin film, as estimated from the calibration (Fig. 4(c)). On the basis of the standard deviations of the slope and intercept in the calibration, the expected thickness of the silver thin film was 43.9–56.7 nm.

A silver thin film was formed on the core of an optical-fiber tip by stopping the silver mirror reaction when the absorbance value reached 1.25. The prepared fiber tip was immersed in water. The reflectance intensity before and after immersion is shown in Fig. 5(a). When the fiber tip was immersed into water, a decrease in the reflectance intensity, compared with that of a fiber tip not immersed in water, was observed at wavelengths from 500 to 800 nm. To obtain the SPR spectra, the ratio of the reflectance intensity of water to that of air, *i.e.* before immersion, was estimated from Fig. 5(a). The decrease in SPR was observed at ~600 nm (Fig. 5(b)). The shape of the spectrum and the wavelength of the SPR dip were approximately the same as those previously reported.²⁵

Evaluation of the sensor probe by measuring sucrose solutions

SPR sensors are based on the detection of changes in the refractive index, and measurements of the reflective index of sucrose allow us to evaluate the performance of the SPR sensors. The performance of the fabricated sensor probe was evaluated by measuring sucrose solutions with concentrations ranging from 0 to 16% (w/v) (Fig. 6(a)). When a blank sample without sucrose was measured, an SPR dip was observed at ~600 nm. The SPR dip shifted to longer wavelengths with increasing concentration of sucrose. The differences in the wavelength of the SPR dip between the water and sucrose solutions were plotted against the sucrose concentration, resulting in a highly linear plot ($R^2 = 0.999$) (Fig. 6(b)). The sensitivity of the sensor calculated using the refractive index values of sucrose solutions was 2205 nm/RIU in the refractive index range from 1.333 to 1.357. The sensitivity of the present SPR sensor is similar to that of sensors fabricated using other methods.^{26–33} The relative standard deviation (RSD) ($n = 3$) was estimated to be less than

Fig. 4 Relationship between the absorbance value and the thickness of a silver thin film. (a) Silver thin film formed by a vacuum thermal evaporation method. (b) AFM image of a silver-coated optical fiber after the removal of a small part of the silver thin film. (c) Relationship between the absorbance and thickness measured by AFM.

Fig. 5 SPR spectra of a silver-coated optical fiber prepared using the developed technique. (a) The reflected-light spectra obtained by measuring in air and underwater. (b) SPR spectrum obtained from the ratio of the reflected light intensity measured underwater to that measured in the air.

Fig. 6 Performance of the SPR sensor prepared using the developed technique. (a) SPR spectra obtained from measuring sucrose solutions with different concentrations lower than 16% (w/v). (b) Calibration curve for sucrose ($n = 3$).

3.3%.

The performance among different SPR sensor probes prepared by the silver-mirror reaction was investigated by measurements of sucrose solutions (Fig. S4, Supporting Information). Nearly the same linear relationship was obtained with the four fabricated FO-SPR sensor probes. The obtained sensitivity and the RSD ($n = 4$) were estimated to be 2600 nm/RIU and <4.2%, respectively. These results reveal that the present method enables the fabrication of sensor probes with excellent reproducibility. The slight difference in the measured values may be due to small variations in the thickness of the fiber probes.

Conclusions

We demonstrated that transmittance measurements of silver thin films enable real-time monitoring of the film thickness. Using this approach, we developed a real-time monitoring system for the thickness of silver thin films on fiber cores; the dynamic range of the system was 30 – 60 nm. The system was used to study the deposition of a silver film onto a fiber core at a given thickness, enabling the fabrication of an FO-SPR sensor whose performance is comparable to that of sensors prepared using other techniques. The approach proposed here has the advantage that the change in the thickness of thin film on the target object can be monitored directly. Therefore, our system is an especially powerful tool for controlling the thickness of thin films deposited by electroless plating techniques, rather than by physical methods, such as vacuum evaporation and sputtering.

References

1. P. J. D. Whiteside, J. A. Chininis, and H. K. Hunt, *Coatings*, **2016**, 6, 35.
2. M. EL Shabasy, M. A. EL Hiti, and M. A. Ahmed, *J. Mater. Sci.*, **1990**, 25, 585.
3. H.-L. Chen, Y.-M. Lu, and W.-S. Hwang, *Mater. Trans.*, **2005**, 46, 872.
4. A. Jilani, M. S. Abdel-wahab and A. H. Hammad, "Advance Deposition Techniques for Thin Film and Coating, *Modern Technologies for Creating the Thin-film Systems and Coatings*", **2017**, N. N. Nikitenkov, IntechOpen, London.
5. Y. B. Chauhan, *IJSRD*, **2015**, 2, 161.
6. K. Niitsu, S. Ota, K. Gamo, H. Kondo, M. Mori, and K. Nakazato, *IEEE Trans. Biomed. Circuits Syst.*, **2015**, 9, 607.
7. Y. Lei, H. Chen, H. Dai, Z. Zeng, Y. Lin, F. Zhou, and D. Pang, *Biosens. Bioelectron.*, **2008**, 23, 1200.
8. H. G. Tompkins, S. Tasic, J. Baker, and D. Convey, *Surf. Interface Anal.*, **2000**, 29, 179.
9. J. Toudert, *Nanotechnol. Rev.*, **2014**, 3, 223.
10. H. Takahara, *Rigaku Journal*, **2017**, 33, 17.
11. A. Carapelle, K. Fleury-Frenette, J.-P. Collette, H.-P. Gamirand P. Harlet, *Rev. Sci. Instrum.*, **2007**, 78, 123109.
12. L. Vera-Londono, O. Caballero-Calero, J. A. Pérez-Taborda, and M. Martín-González, "Advances in Scanning Thermal Microscopy Measurements for Thin Films, Coatings and Thin-Film Technologies", J. A. Perez-Taborda, and A. G. A. Bernal, **2018**, IntechOpen, London.
13. Y. Gan, *Surf. Sci. Rep.*, **2009**, 64, 99.
14. A. Mohammed, and A. Abdullah, Scanning Electron Microscopy (SEM): A Review, *Proc. of 2018 ICHP-HERVEX*, 2018, Romania.
15. M. Liszewska, M. Stefaniak, J. Firak, B. Bartosiewicz, B. Budner, T. Wojciechowski, B. J. Jankiewicz, and P. Nyga, *Proc. of 2014 16th ICTON*, IEEE, 2014, Austria.
16. A. Axelevitch, B. Gorenstein, and G. Golan, *Physics Procedia*, **2012**, 32, 1.
17. V. Lozanova, A. Lalova, L. Soserov, and R. Todorov, *J. Physics*, **2014**, 514, 012003.
18. R. C. Jorgenson and S. S. Yee, *Sens. Actuators, B*, **1993**, 12, 213.
19. C. Desmet, K. Vindas, R. A. Meza, P. Garrigue, S. Voci, N. Sojic, A. Maziz, R. Courson, L. Malaquin, T. Leichle, A. Buhot, Y. Roupiez, L. Leroy, and E. Engel, *Sensors*, **2020**, 20, 511.
20. Q. Liu, Y. Liu, S. Chen, F. Wang, and W. Peng, *Sensors*, **2017**, 17, 2797.
21. S. Singh, R. K. Verma and B. D. Gupta, *Opt. Quant. Electron.*, **2010**, 42, 15.
22. Y. Liu, Q. Liu, S. Chen, F. Cheng, H. Wang, and W. Peng, *Sci. Rep.*, **2015**, 5, 12864.
23. N. Parvini-Ahmadi and M. A. Khosravipour, *Int. J. ISSI*, **2004**, 1, 29.
24. Y. Saito, J. J. Wang, D. N. Batchelder, and D. A. Smith, *Langmuir*, **2003**, 19, 6857.

25. Y. Zhao, Z. Deng, and Q. Wang, *Sens. Actuators, B*, **2014**, 192, 229.
 26. Z. Mai, J. Zhang, Y. Chen, J. Wang, X. Hong, Q. Su, and X. Li, *Biosens. Bioelectron.*, **2019**, 144, 111621.
 27. P. Hlubina, M. Kadulova, D. Ciprian, and J. Sobota, *J. Europ. Opt. Soc. Rap. Public.*, **2014**, 9, 14033.
 28. Q. Liu, H. Yuan, Y. Liu, J. Wang, Z. Jing, and W. Peng, *J. Biomed. Opt.*, **2018**, 23, 047003.
 29. H. Suzuki, M. Sugimoto, Y. Matsui, and J. Kondoh, *Sens. Actuators, B*, **2008**, 132, 26.
 30. J. Zhao, S. Cao, C. Liao, Y. Wang, G. Wang, X. Xu, C. Fu, G. Xu, J. Lian, and Y. Wang, *Sens. Actuators, B*, **2016**, 230, 206.
 31. S. Shi, L. Wang, R. Su, B. Liu, R. Huang, and W. Qi, Z. He, *Biosens. Bioelectron.*, **2005**, 74, 454.
 32. S. Shi, L. Wang, A. Wang, R. Huang, L. Ding, R. Su, and W. Qiade, Z. He, *J. Mater. Chem. C*, **2016**, 4, 7554.
 33. T. Hu, Y. Zhao, and A. Song, *Sens. Actuators, B*, **2016**, 237, 521.
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