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Properties of a gold-deposited surface plasmon resonance-based glass rod sensor with various light-emitting diodes and its application to a refractometer

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ABSTRACT

The performance of a simple sensor system prepared using gold (Au)-deposited glass rods of 1 to 4 mm in diameter with a deposition length of 100 mm based on surface plasmon resonance (SPR) is presented. The sensor properties of the Au-deposited glass rods of 2 mm in diameter with deposition lengths of 10 to 100 mm are also presented. The sensor system consists of a light-emitting diode (LED) as the light source and a photodiode (PD) as the detector. The response curves and sensor properties of the Au-deposited glass rod with a Au film thickness of 45 nm obtained by using three LEDs with yellowish green (563 nm), red (660 nm), and infrared (940 nm) emissions were investigated. The results were compared with those of a corresponding Au-deposited optical fiber sensor with a core diameter of 0.2 mm. Though the sensitivity, response, and detection limit of the Au-deposited glass rod sensor are lower than those of the optical fiber sensor, the fabrication and handling of the Au-deposited glass rod sensor are easier because of the robustness. Since the dielectric constant of Au changes with the light wavelength, the sensor properties of both the Au-deposited glass rod sensor and the optical fiber sensor depend strongly on the wavelength of the incident light and can be controlled by changing the LED emission wavelength. This sensor system is a new SPR-based refractometer with easy construction and operation. Ethanol concentrations in various spirits were measured with this SPR-based refractometer and the results agreed well with those measured with an Abbe refractometer.

1. Introduction

An optical fiber sensor system based on surface plasmon resonance (SPR) allows the development of remote sensing, continuous analysis, and *in situ* monitoring with an inexpensive and disposable sensor element [1–3]. Such sensor systems enable determination of the refractive index (RI) of a sample with high accuracy. Gold (Au) and silver (Ag) are the most widely used metals for the sensor elements. The sensor properties depend on the dielectric constant ($\varepsilon_r + \varepsilon_i\ i$) of the deposited metal [4–7]. Sensor systems having a sensor element of a deposited metal film on the core of a multi-mode optical fiber have been developed for scanning wavelengths [8–17] and for changing the angle of incident light [18–28]. These systems need a spectrometer or a precision rotator. Another type of sensor with a thin deposited metal film on the core of a side polished single-mode optical fiber implanted in a silica block has been reported [29–37]. In this system, the incident light is guided into the sensor through a polarizer and a polarization controller without the need to scan the wavelength or change the incident angle. This type of sensor has high resolution because of an optimal bend in the single-mode optical fiber. However, the fabrication of the sensor element and the optics of the system are complicated. A small and simple sensor system is desirable in SPR sensing applications.

We have previously developed a small and simple Au-deposited multi-mode optical fiber sensor, in which the core of the optical fiber having a diameter of 0.2 mm was coated entirely with a Au film, and the light intensity of a He–Ne laser (632.8 nm) transmitted through the sensor was measured without scanning the wavelength or changing the angle of the incident light [38–43]. The sensor properties were evaluated by analyzing the responses for various samples [38–43]. We then simplified the structure of the sensor element of the Au-deposited optical fiber sensor by depositing the Au film on only half of the core of the optical fiber with a geometric thickness distribution [44]. This simplified sensor element exhibits better properties than those of our previous sensor elements [44]. Furthermore, we also fabricated metal-deposited optical fiber sensors using Cu and Al, and

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reported their response curves and sensor properties for the first time [45]. The sensor properties of the Al-deposited and Ag-deposited SPR optical fibers were studied thoroughly along with the surface characterization of these metal films by atomic force microscopy and X-ray photoelectron spectroscopy [46,47]. Recently, we presented a simple sensor system using the Au-deposited optical fiber sensor in which a light-emitting diode (LED) and a photodiode (PD) were employed as the light source and the detector, respectively [48]. These sensor systems promise the development of a new analytical technique for use in SPR sensing applications.

In the present paper, we report a simple sensor system using a Au-deposited SPR glass rod as the sensor element. The great advantage of the Au-deposited SPR glass rod over the Au-deposited optical fiber is its robustness. The Au films of the sensor elements were deposited on only half of the glass rods of 1–4 mm in diameter with a deposition length of 100 mm. The sensor properties of the Au-deposited glass rods of 2 mm in diameter with deposition lengths of 10–100 mm were also investigated. The fabrication and handling of the Au-deposited glass rod were both found to be easier than those of the Au-deposited optical fiber, and thus the sensor element is of practical use. The system consists of an LED as the light source, a sensor cell containing the sensor element in it, and a PD as the detector. The LED and PD can be arranged directly on both ends of the Au-deposited SPR glass rod. Since the dielectric constant of Au changes with the wavelength of light, the sensor properties depend strongly on the wavelength, and these properties can be controlled by changing the LED emission wavelength. The response curves and sensor properties of the Au-deposited glass rod with a maximum Au film thickness of 45 nm produced using three LEDs having different emission wavelengths (563, 660, and 940 nm), were investigated and compared with those of our Au-deposited optical fiber sensor [48]. The usefulness and application of the Au-deposited SPR glass rod sensor system as a refractometer are demonstrated by an analysis of ethanol in various spirits.

2. Experimental

A schematic representation of the sensor cell containing the Au-deposited glass rod and the sensor system is shown in Fig. 1. The sensor elements were prepared by vacuum evaporation of Au films on silicate glass rods (Vidtec, 1, 2, and 4 mm in diameter and 150 mm in length, refractivity: 1.464 ± 0.001 RI unit). The Au films with a thickness of 45 nm were deposited on half of the clean glass rods by evaporation of Au (Ishifuku Metal, > 99.99%) at a rate of 1.0 nm/s in a high vacuum ($< 6 \times 10^{-4}$ Pa) at room temperature. The deposited Au film on the glass rod has a geometric thickness distribution in which the maximum value (45 nm) represents the thickness of the deposited metal [44,45]. The uncertainty of the Au thickness was less than 0.2 nm. The sensor element and Teflon tubes used as sample inlets and outlets were fixed in a glass tube (5 or 6 mm in diameter and 120 mm in length) with resin to form a sensor cell. Methanol solutions of ethylene glycol or benzyl alcohol, or aqueous solutions of ethanol maintained at 25 °C, were then allowed to flow through the sensor cell.

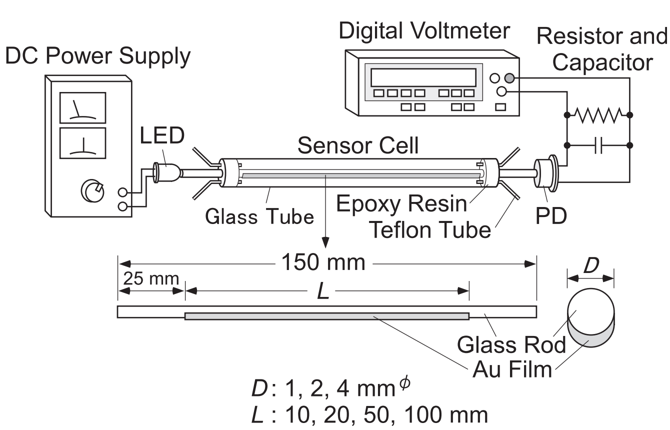

Fig. 1. Schematic representation for the experimental setup of the Au-deposited SPR glass rod sensor system comprising a light-emitting diode (LED) light source, a photodiode (PD) detector, and a sensor cell containing a sensor element and a sample solution maintained at 25 °C flowing through it. The sensor elements are the Au-deposited SPR glass rods of 1–4 mm in diameter (*D*) with deposition lengths (*L*) of 10–100 mm.

An end of the glass rod of the sensor element was illuminated with an LED and the light intensity transmitted through the sensor was converted to a dc current with a PD (Hamamatsu S2386-44K). The optical characteristics of the LEDs used for the sensor system are shown in Table 1. The PD exhibited sensitivity to wavelengths from 320 to 1100 nm. The dc current was converted to voltage using a resistor (10 kΩ) and measured with a digital voltmeter (Kikusui 1502). A capacitor (4.7 μF) was used to reduce background noise. The light intensity was also measured and converted to digital data using a digital multimeter (Yokogawa 755501-1) used as an A/D converter and then monitored with a computer (PC/AT Compatible). The light intensity was measured with a mini-spectrometer (Hamamatsu C10083MD, wavelength resolution: 8 nm) to investigate broadening of the response curves due to the wavelength widths of the LEDs used. The refractivities of the samples were measured with an Abbe refractometer (Atago DR-A1 or RX-5000α-Bev) and the uncertainties were less than 2×10^{-4} or 4×10^{-5} RI unit, respectively.

3. Results and discussion

3.1. Response curves of the Au-deposited glass rod

Fig. 2 shows the response curves of the Au-deposited glass rod sensors of 2 mm in diameter with a deposition length of 100 mm and with a film thickness of 45 nm, measured using three different LEDs as the light source for methanol solutions of ethylene glycol maintained at 25 °C in the refractivity range from 1.327 to 1.431 RI unit. The transmitted light intensities for the solutions were measured and normalized by those obtained for the solvent (methanol) at 1.327 RI unit. The refractivities at the minima in the response curves of the sensor are shown in Table 2. The values of the refractivities at the minima are obtained using the second order curves and are averages of those of three or four response curves for different measurements of the sensors. Uncertainty values are standard deviations (< 0.003 RI unit). The corresponding values of the Au-deposited optical fiber sensors with the same LEDs [48] are shown in Table 3. The refractivities at the minima in the response curves of the Au-deposited glass rod sensors are smaller (0.004–0.006 RI unit) than

Table 1
Optical characteristics of the LEDs used for the Au-deposited SPR glass rod sensor system.

Manufacturer and product number	Emission color	Peak wavelength (nm)	Peak width (FWHM) (nm)
Rohm SLA-560MT	Yellowish green	563	40
Rohm SLA-560LT	Red	660	25
OptoSupply OSIR5113A	Infrared	940	51