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Molecular selectivity development of Teflon® AF1600-coated gold-deposited surface plasmon resonance-based glass rod sensor

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ABSTRACT

A gold (Au)-deposited surface plasmon resonance (SPR)-based glass rod sensor coated with an α-mercaptoethyl-ω-methoxy polyoxyethylene (PEG thiol) layer and a Teflon AF1600 overlayer with high selectivity for small molecules in aqueous solutions was developed. The PEG thiol layer forms a space (approximately 13 nm thick) for analytes between the Au film (45 nm thick) and the Teflon layer (25 μm thick). Small molecules in sample solutions pass selectively through the porous Teflon, accumulate in the PEG thiol layer and are detected using the SPR phenomenon. PEG thiol adsorption on the Au films was confirmed by the sensor response and X-ray photoelectron spectroscopy. Teflon overlayer thicknesses on the Au films were measured using cross-sectional scanning electron microscope images of the sensor. The sensor's selectivity was evaluated using aqueous solutions of methanol, ethanol, propanol, ethylene glycol, glycerin, pentaerythritol, and glucose. Only the monohydric alcohols pass through the Teflon overlayer, while the polyhydric alcohols do not pass through the layer. This sensor thus allows us to measure the ethanol concentrations directly in aqueous ethanol solutions mixed with interference compounds. The sensor is unaffected by glucose, tartaric acid, and glutamic acid in the solutions.

1. Introduction

Surface plasmon resonance (SPR) sensor systems use metal films deposited on bulk prisms or optical waveguides, and use an optical phenomenon in which incident light excites charge density waves at the interface between the metal and a dielectric [1–5]. The resonance angle or the wavelength at which the coupling of the incident light and the surface plasmon waves occurs depends on both the dielectric constant of the deposited metal and the refractive index of the sample. Because the SPR sensor system only responds to the refractive index of the sample under test, many researchers have attempted to add selectivities for specific analytes to these systems [1–3,6–15]. Combination of the SPR sensor with a biochemical reaction, e.g., an antigen–antibody reaction or an enzyme reaction, allows the detection of specific molecules [1–3,7,12]. Selective layers for the SPR sensing elements using an acid–base reaction [10], complex formation between an ionophore and a metal ion [11,13], molecularly imprinted polymers [8,9,15], and diffusion in agar [14] were also investigated. However, these biochemical and chemical selective layers have short lifetimes because they degenerate.

Teflon AF1600 and AF2400, commercialized by Du Pont Co., Ltd. [16], are random copolymers of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole [17–23]. They are glassy materials with large free volumes that are attributed to the amorphous parts formed by the dioxole units in the chemical structures [17]. They have extremely high gas permeability and are characterized by very large free volumes with radii of 3–8 Å [18,21]. Therefore, Teflon AF1600 and AF2400 are used as molecular sieves for sensing elements. Kurauchi et al. [24] fabricated a fiber-optic ethanol sensor coated with a chitosan/poly (vinyl alcohol) blended polymer membrane and a Teflon AF1600 overlayer. The Teflon layer allows the ethanol to be separated from shochu, sake, wine, whiskey, and beer. This sensor measures changes in the light intensity passing through the optical fiber as a result of an increase in the fiber critical angle caused by ethanol, which was induced by shrinkage of the chitosan/poly (vinyl alcohol) blended membrane. The refractive indices of the thin AF1600 and AF2400 membranes are 1.31 and 1.29 refractive index (RI) units, respectively, and are lower than those of any other polymers [16]. This means that AF1600 and AF2400 can effectively be used as selective layers for the SPR sensing element. Podgorsek et al. [25–27] studied a silver-based SPR sensing element using the AF1600 thin film as a sensitive layer for aromatic vapors of benzene, toluene, and xylene. They calculated the diffusion coefficients of these aromatic vapors in

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the AF1600 film. Erickson et al. [28] reported a gold-based near-infrared SPR sensing system with an oxygen plasma-etched Teflon AF1600 selective layer to detect benzene, toluene, and xylene in water. They demonstrated detection limits for benzene, toluene, and xylene of 183, 105, and 55 parts per billion (ppb), respectively.

We previously developed a small and simple Au-deposited multimode optical fiber sensor, in which the light intensity of a He–Ne laser (632.8 nm) that was transmitted through the sensor was measured without scanning of the wavelength or variation of the angle of incidence of the light [29–40]. Another simple sensor system using Au-deposited glass rods with diameters of 1–4 mm and deposition lengths of 10–100 mm equipped with a light-emitting diode (LED) has also been presented [41,42]. The response properties of these metal-deposited optical fiber and glass rod sensors could be controlled by varying the metal thickness [32–35,40], the type of metal used [36–38,40], and the incident light wavelength [39–41]. Recently, we have developed a Teflon AF1600-coated Au-deposited SPR-based optical fiber sensor [43]. This sensor allows us to measure ethanol concentrations directly in shochu, sake, and wine. Experiments showed that the ethanol concentrations could be measured directly in a mixture containing glucose or tartaric acid. The ethanol solution sensitivity of the sensor was enhanced by adding an α-mercaptoethyl-ω-methoxy polyoxyethylene (PEG thiol) spacer layer between the Au film and the Teflon selective layer.

This paper describes in detail the response properties of a Teflon AF1600-coated Au-deposited SPR-based glass rod sensor. The adsorption behavior of the PEG thiol layer on the Au films and the morphology of the Teflon AF1600 film on the SPR glass rod sensor are also discussed. The PEG thiol adsorption behavior was monitored using the response of the sensor without the Teflon layer to an ethanol solution of PEG thiol. The adsorption and monolayer formation of PEG thiol on the Au films [44–47] was also confirmed using X-ray photoelectron spectroscopy (XPS). The formation of the Teflon overlayers on the sensors was observed by scanning electron microscopy (SEM) and the layer thicknesses were measured from their cross-sectional images. The responses of the Teflon AF1600-coated Au-deposited SPR-based glass rod sensor to aqueous ethanol solutions were observed. The sensor's selective properties were evaluated using aqueous solutions of methanol, ethanol, propanol, ethylene glycol, glycerin, pentaerythritol, and glucose. The sensor allows us to perform direct measurements of the ethanol concentrations of aqueous ethanol solutions mixed with glucose, tartaric acid, and glutamic acid. The results demonstrated the value of the Teflon AF1600-coated Au-deposited SPR glass rod sensor with molecular size selectivity.

2. Principle

Fig. 1 shows a schematic representation of the response principle of the Teflon AF1600-coated Au-deposited SPR glass rod sensor. The chemical structures of PEG thiol and Teflon AF1600 are also shown. The sensing element has a silicate glass rod/Au film/PEG thiol spacer layer/Teflon AF1600 overlayer structure. Teflon AF1600 is composed of amorphous random copolymers of 65 mol% 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and 35 mol% tetrafluoroethylene, and exhibits strong hydrophobicity. The radii of the free volume elements in the Teflon AF film are in the 3–8 Å range [18,21]. The Teflon AF film shows size-sieving properties and high gas and liquid permeability because of its large free volume [17–23].

It is well known that thiol forms a self-assembled monolayer on Au [44–47]. The PEG thiol layer acts as a hydrophilic spacer between the Teflon AF1600 overlayer and the Au film [43]. Thus, the small hydrophilic molecules that have been selected by the Teflon

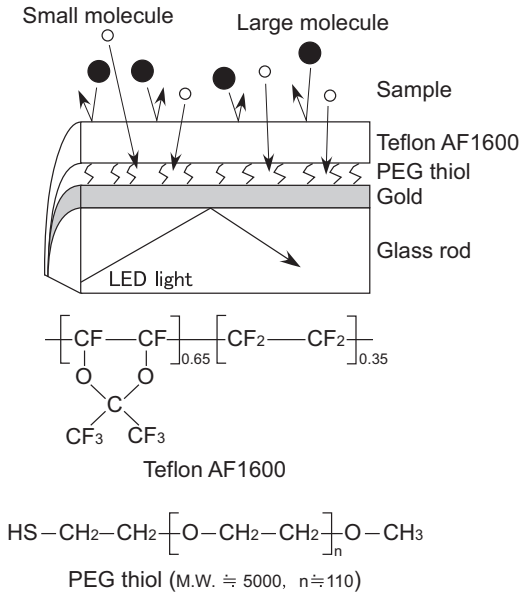

Fig. 1. Schematic representation of the response principle of the Au-deposited SPR glass rod sensor coated with an α-mercaptoethyl-ω-methoxy polyoxyethylene (PEG thiol) layer and a Teflon AF1600 overlayer. Small molecules in the sample solution pass through the porous structure of the Teflon AF1600 selective layer with the thickness of 25 μm, and they accumulate in the PEG thiol spacer layer with the thickness of 13 nm. The accumulated small molecules are detected selectively and sensitively via the SPR phenomenon on the Au film deposited on the silicate glass rod.

layer accumulate in the PEG thiol spacer layer and are detected as a change in the refractive index of the layers through the SPR phenomenon on the Au film deposited on the silicate glass rod.

3. Experimental

The preparation of the Au-deposited SPR glass rod sensor elements has been reported previously [41,42]. The Au film with a thickness of 45 nm was deposited on half of the clean silicate glass rod (2 mm diameter × 140 mm long, Vidtec, Fukuoka, Japan) by Au (>99.99%, Ishifuku Metal, Tokyo, Japan) evaporation at a rate of 1.0 nm/s in a high vacuum ($<6 \times 10^{-4}$ Pa) at room temperature. The Au film deposited on the glass rod has a geometrical thickness distribution in which the maximum value (45 nm) represents the deposited metal thickness [35–43]. The uncertainty of the Au film thickness was less than 0.3 nm. The Au-deposited glass rod was then immersed into a 0.1 mM ethanol solution of PEG thiol (ME-050SH, MW: 5,000, NOF Corporation, Tokyo, Japan) for 1 h to form the spacer layer. After the adsorption of PEG thiol on the Au film of the Au-deposited glass rod, the rod was washed thoroughly with ethanol and dried for 30 min in the air. Finally, the Au-deposited glass rod with the adsorbed PEG thiol layer was coated with a Teflon overlayer, which was fabricated by either five or six repeated cycles of immersion of the Au-deposited glass rod into a 35 mg/ml Fluorinert (FC-72, Sumitomo 3 M, Tokyo, Japan) solution of Teflon AF1600 (DuPont, Wilmington, Delaware, USA) followed by drying for 1 min. The sensor element and the Teflon tubes that were used as the sample inlets and outlets were fixed in a glass tube (5 or 6 mm diameter, 120 mm long) with resin to form a sensor cell. Sample solutions at 25 °C were then allowed to flow through the sensor cell.

One end of the glass rod of the sensor element was illuminated using an LED (SLA-560LT, 654 nm emission wavelength, Rohm, Kyoto, Japan) and the transmitted light intensity through the sensor was monitored using either a photodetector (S2386-44K, Hamamatsu Photonics, Shizuoka, Japan) or an optical multimeter