別記様式第３号－１

学 位 論 文 の 要 旨	
氏　　　名	増永　卓朗
学位論文題目	金蒸着ガラス棒表面プラズモン共鳴センサー装置の高性能化と センサーのテフロン被覆による選択性の付与に関する研究

本論文は，　金蒸着ガラス棒表面プラズモン共鳴(SPR)センサー装置の高感度化と性能評価，その応答特性のフレネル方程式を用いた理論解析，およびセンサー素子のテフロン被覆によるアルコール選択性の付与についてまとめたものである。

第１章では, SPR現象を説明し, 金蒸着ガラス棒SPRセンサー装置の利点を挙げる。さらに第２章以降の研究成果の概要について説明した。

第２章は，発光ダイオード(LED)を光源とするSPR現象に基づいた金蒸着ガラス棒SPRセンサー装置における高感度化に関する研究である。参照光の強度を用いて応答信号を規格化することによって，応答の安定性が向上し，より微小な屈折率変化を測定することが可能になった。エタノール水溶液，ベンジルアルコールのメタノール溶液，2-プロパノールのエタノール溶液の検出限界の測定を行い，それぞれ 4.8×10^{-5} RIU，4.5×10^{-5} RIU，5.2×10^{-5} RIUの屈折率変化を検出した。これらの結果は，本研究室のLEDを用いる従来の金蒸着ガラス棒SPRセンサーと比較して約4倍の高感度化を達成しており，また本研究室のレーザーを光源とする金蒸着光ファイバーSPRセンサーと同程度の性能である。NaCl，KCl，$MgCl_2$，$CaCl_2$ 水溶液の濃度測定を行った結果，1.8×10^{-5} RIU，1.3×10^{-5} RIU，6.1×10^{-6} RIU，8.9×10^{-6} RIUの検出限界であった。以上の成果により，本金蒸着ガラス棒SPRセンサー装置において，目的とする性能向上が達成されたことを実証した。

第３章では，金蒸着ガラス棒SPRセンサーの応答特性について，フレネル方程式を用いた理論的な応答予測について研究した。平板におけるSPR応答のフレネル方程式を金蒸着ガラス棒SPRセンサーに適用するために，LEDの入射光強度分布，ガラス棒内の入射角分布，蒸着金の形状による膜厚分布，蒸着金の長さ，ガラス棒の直径を考慮した。その結果，金蒸着ガラス棒SPRセンサーの応答曲線の最小値のピーク位置と幅は，実験と理論の両方において実験誤差の範囲内で良く一致し，フレネル方程式を用いた金蒸着ガラス棒SPRセンサーの理論による性能予測の有用性を示した。

第４章では，センサー素子のテフロンAF2400膜被覆による金蒸着ガラス棒SPRセンサーへのアルコール選択性の付与について研究を行った。テフロンAF膜は結晶質と非結晶質のランダムな共重合体であり，非結晶質において半径3～8Åの微細孔があるために高いガス透過性を持っている。この微細孔による分子サイズのふるい分けによりセンサーに選択性を付与することができる。妨害物としてグルコースを溶解させたエタノール水溶液を，テフロンAF2400選択膜で被覆した金蒸着ガラス棒SPRセンサーを用いて測定を行った結果，グルコースを排除しエタノール濃度のみを検出することができた。このセンサーを用いて各種の蒸留酒や醸造酒のアルコール濃度の直接測定が可能であり，分離と検出の機能を併せ持つセンサーを開発することができた。

第５章では，金蒸着ガラス棒SPRセンサーに関する本研究成果を総括した。本センサー装置は簡便であるにもかかわらず，既存の高感度な屈折率装置に匹敵する性能である。またその応答特性をフレネル方程式を用いた理論計算で予測することができる。さらに，テフロンAF選択膜の被覆により試料の分離と検出を併せ持つセンサーであることを実証した。これらの成果より，金蒸着ガラス棒SPRセンサーの性能向上と応答特性の理論による予測，さらに選択性を持つセンサー素子の開発などの分析化学の分野における学術性と実用性が実証された。

別記様式第４号

Summary of Doctoral Dissertation

Title of Doctoral Dissertation:

Studies on Improvement of a Gold-deposited Surface Plasmon Resonance-based Glass Rod Sensor System and Selectivity Development of the Sensor by Teflon Coating

Name: Masunaga Takuro

This thesis mainly comprises 5 chapters.

Chapter 1 gives the introduction of a surface plasmon resonance (SPR) phenomenon and the principle of a gold (Au)-deposited SPR-based glass rod sensor. The SPR phenomenon is a resonance between an evanescent wave of incident light and a surface plasmon wave in a metal film deposited on a prism or a waveguide. 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 solution. The Au-deposited SPR-based glass rod sensor system has been used. The light intensity of a light emitting diode (LED) that is transmitted through the sensor is measured without scanning of either the wavelength or the variation of the angle of incidence of the light in the system. In the present thesis, the improvement of the sensitivity of the Au-deposited SPR-based glass rod sensor system is described. The sensor properties are estimated from the response curves of the sensors calculated using a three-layer Fresnel equation. The coating of the sensor element with a Teflon AF2400 overlayer gives the high selectivity for small molecules contained in aqueous solutions.

In Chapter 2, the improvement of the Au-deposited SPR-based glass rod sensor system is described. The sensor system consists of a LED with a wavelength of 654 nm as the light source and a photo diode (PD) as the detector and the reference. A high sensitivity and a stable baseline were obtained using the signal normalization by the reference. Detection limits for an aqueous ethanol solution, a methanol solution of benzyl alcohol, and an ethanol solution of 2-propanol were 4.8×10^{-5} RIU, 4.5×10^{-5} RIU, and 5.2×10^{-5} RIU, respectively. The sensitivity of the improved sensor system is about 4 times higher than that of our previous sensor system using a LED, and also it is the same as that of our sensor system using a laser as the light source. Detection limits for aqueous solutions of NaCl, KCl, and $MgCl_2$, $CaCl_2$ were 1.8×10^{-5} RIU, 1.3×10^{-5} RIU, and 6.1×10^{-6} RIU, 8.9×10^{-6} RIU, respectively.

In Chapter 3, the response curves of Au-deposited SPR-based glass rod sensors were calculated using a three-layer Fresnel equation while considering various parameters for the sensor system calculations. Au films with thicknesses of 30, 45, and 70 nm were deposited on half of the surfaces of the glass rods, which were 2 mm in diameter, with a deposition length of 100 mm. Sensor elements with Au film thicknesses of 45 nm on glass rods with diameters of 1 and 4 mm and with deposition lengths of 10, 20, and 50 mm were also prepared. The sensor system consists of a LED with a wavelength of 654 nm as the light source with a mini-spectrometer as the detector. The LED intensity distribution, the range of

the angle of incidence of light into the sensor element, and the thickness distributions of the Au films deposited on the glass rods were considered to be the important parameters for the calculations. The minimum positions of all the theoretical response curves agreed well with those of the experimental response curves within the limits of the experimental and theoretical uncertainties. Most of the overall response characteristics of the theoretical curves agreed well with those of the experimental curves within the limits of both types of uncertainty. It was found that the thickness distribution of the deposited Au film in the cross-sectional direction dominates the sensor response and thus is the most important parameter for calculation of the sensor properties. The agreements between the experimental and theoretical response curves indicate both the potential and the usefulness of the sensor performance estimation process based on the three-layer Fresnel equation.

In Chapter 4, a Au-deposited SPR-based glass rod sensor coated with an α-mercaptoethyl-ω-methoxy polyoxyethylene (PEG thiol) layer and a Teflon AF2400 overlayer with high selectivity for small molecules contained in aqueous solutions was developed. The PEG thiol layer forms a space (approximately 13 nm wide) for the analytes to accumulate between the Au film (45 nm thick) and the Teflon layer (approximately 12 μm thick). The water and alcohol content in the sample solutions pass selectively through the porous Teflon overlayer, accumulate in the PEG thiol spacer layer and are then detected through the SPR phenomenon. Cross-sectional scanning electron microscope imaging of the sensor was used to measure the thickness of the Teflon overlayer on the Au film. The sensor selectivity was then evaluated using aqueous solutions of various alcohols. The sensor responds reversibly to the concentrations of only monohydric alcohols. The response is faster than that of the Teflon AF1600-coated sensor as a result of the increased permeability and the reduced thickness of the Teflon AF2400 overlayer. The sensor maintains both its sensitivity and its selectivity for as long as 6 months. Direct measurement of the ethanol concentrations of aqueous ethanol solutions that were mixed with interference compounds is possible using this sensor. The ethanol concentrations of various liquors were measured directly. This sensor is a unique device with functions for both separation and detection of the analytes.

Chapter 5 is the conclusion. The improved Au-deposited SPR-based glass rod sensor system consists of a LED with a wavelength of 654 nm as the light source and a photo diode (PD) as the detector and the reference. The high sensitivity and a stable baseline were obtained using the signal normalization by the reference. The present sensor system with the detection limit of the order of 10^{-5} RIU is simple and well comparable with a high-performance commercial refractometer.

The response curves of the sensors can be calculated using a three-layer Fresnel equation while considering various parameters for the sensor system. The thickness distribution of the deposited Au film in the cross-sectional direction is the most important parameter for calculation of the sensor properties.

The coating of the sensor element with a PEG thiol spacer layer and a Teflon AF2400 overlayer gives the high selectivity for small molecules contained in aqueous solutions. This sensor allows us to measure ethanol concentrations directly in aqueous ethanol solutions mixed with interference compounds. The ethanol concentrations of various liquors were measured directly. The sensor is a unique device with functions for both separation and detection.

The present studies demonstrate the usefulness of this improved Au-deposited SPR-based glass rod sensor system in science and engineering.