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Control of the dynamic range and sensitivity of a surface plasmon resonance based fiber optic sensor

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Abstract

The refractive index sensitivity and dynamic range of a recently developed fiber optic based surface plasmon resonance sensor have been investigated. The sensor response was studied using a set of aqueous refractive index standards. The sensitivity to refractive index was found to be between 5.0×10^{-4} and 5.0×10^{-5} index of refraction units. The dynamic range of an unmodified sensor was between 1.25 and 1.40 index of refraction units. The dynamic range was tuned for ranges between 1.00 and 1.40 index of refraction units with the addition of thin high refractive index overlayer films. This range is significant since it includes both gas and aqueous chemical sample refractive indices. The upper limit of the refractive index dynamic range was extended to 1.70 by use of a sapphire fiber core material.

Introduction

Optical excitation and detection of the surface plasmon resonance (SPR) phenomenon can be used to measure the refractive index of either bulk chemical samples or thin film chemical transducing layers. SPR has been utilized as the transduction mechanism for many chemical sensors. Such sensors include the following: immunoassay [1], liquid [2], gas [1, 3] and thin-film sensors [4]. These sensors have been used to measure antibody concentration, organic solvent concentration, gas concentration, pH and the characterization of thin films, respectively.

SPR has traditionally been applied to chemical sensing using two analytical methods. The first method can be referred to as bulk chemical sensing in which the refractive index of a chemical sample is measured in order to glean information regarding a chemical process. This method has been used to measure both alcohol and sugar concentration in water. The second method utilizes a so called ‘chemical transducing layer’ at the sensor/chemical sample interface. Selectivity and sensitivity enhancement must be designed into the sensor when there are sensing applications involving mixtures and/or small concentrations of analyte. This can be performed by employing selective chemical transducing layers (e.g. selective membrane, chromoionophore, antigen or antibody layers, etc.). A chemical transducing layer implies a thin film which has its optical properties and/or thickness change as a function of the concentration of the analyte to be sensed.

The practical implementation of SPR sensors towards industrial, environmental, biochemical and biomedical sensing has been limited primarily due to the relatively large and expensive bulk optic systems traditionally required. Recently, an SPR fiber optic sensor has been developed that allows for the measurement of the SPR spectrum and has the sensor directly fabricated onto the fiber core. The theory and results of the sensor have been previously reported [5, 6]. The sensor and sensor system, illustrated in Fig. 1, are fundamentally simple in structure, inexpensive and amenable towards remote sensing applications and multiplexing of several fiber sensors.

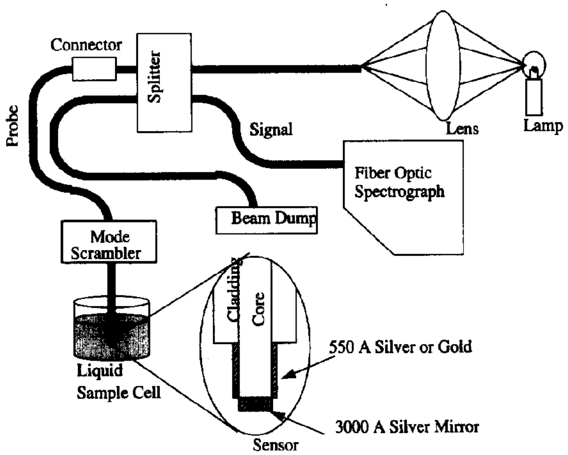

Fig. 1. Illustration of the SPR fiber optic sensor and system.

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The sensor is capable of measuring bulk refractive indices from 1.25 to 1.40. This range is convenient for the measurement of aqueous based processes, such as industrial chemical process monitoring, biochemical processes, and environmental water quality monitoring. However, one may be interested in performing SPR chemical sensing for chemical processes which have real refractive indices outside of the current dynamic range of the sensor. Examples of such chemical samples which have refractive index values outside this range include: gases ($n \approx 1.0$), motor oils ($n \approx 1.46$), corn syrup solutions ($n \approx 1.33$–1.65), epoxies ($n \approx 1.45$–1.75) and fiber glass resins.

This paper will cover two methods in which the dynamic range of the SPR fiber optic sensor may be tuned in order to customize the sensors for specific chemical sensing applications. Furthermore, the sensors may be further optimized to achieve maximum sensitivity for a specific chemical sensor application. The two methods employed require the sensor to be physically modified. The first method employs high refractive index thin films. The second method employs a different fiber optic core material. Such fiber cores commercially available other than fused silica consist of polymethyl methacrylate, PMMA, used in plastic fibers, doped silica fibers, and sapphire.

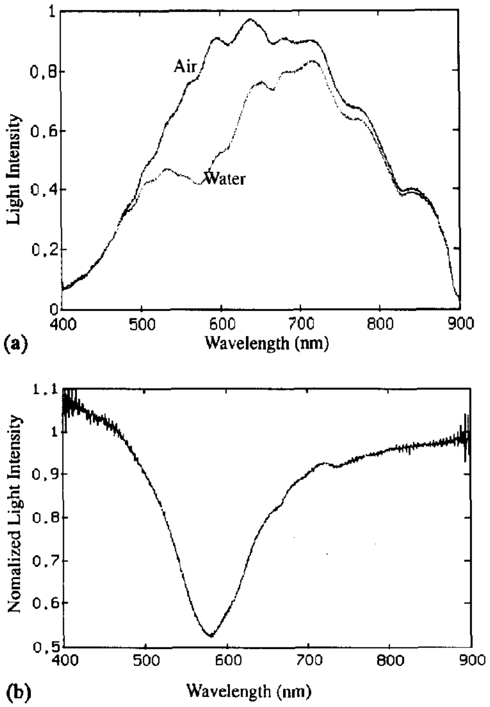

Fig. 2. (a) Measured transmitted light intensity spectrum for when the sensor is in contact with air and water. (b) Normalized transmitted light intensity for water. The spectrum is the ratio of the raw water spectrum divided by the reference air spectrum in (a).

Fiber optic sensor and system

Illustrated in Fig. 1 is a disposable length of optical fiber (400 μm core, multi-mode, 0.36 Numerical Aperture, HCP Ensign-Bickford optical fiber) with an ST style fiber optic connector on one end and the SPR sensing area at the other end. The sensing area is fabricated by first chemically etching off 10 mm of the fiber cladding and buffer layers using hot sulfuric acid. The gold SPR supporting layer (550 Å thick) is symmetrically deposited around the fiber optic via electron-beam evaporation techniques. A mirror is fabricated directly onto the distal tip of the fiber probe by depositing 3000 Å of silver. This probe is connected to an arm of a 2×2 fiber optic splitter. The probe receives approximately 50% of the signal light that is coupled in to the splitter using a lens and a current controlled white light source. The light is transmitted down the probe to the sensing area whereupon the signal light is then reflected back up the fiber by the micro-fabricated mirror. A certain range of wavelengths are attenuated due to the coupling of incident light energy to surface plasmon waves at the gold/chemical sample interface. The returned light is split again and the output leg is connected to a fiber optic spectrograph which is used to measure the spectral intensity of the signal light. The remaining arm of the splitter is index matched to a solution of glycerol so as to minimize back reflection.

Prior to the introduction of the sensor probe to the medium to be sensed, the probe is self-referenced using the following procedure. A transmitted intensity spectrum is measured when the bare gold SPR sensor is in contact with air. This spectrum is a reference spectrum since there is no SPR excitation for air (refractive index of 1.0) within the measured 400–900 nm optical range. Subsequent intensity spectra collected when the probe is in contact with the sensed media will be divided by the reference signal to produce the normalized SPR fiber optic intensity spectrum. This method of referencing allows for the cancellation of any spectral non-uniformities arising from spectral sensitivity, fiber absorbance, grating efficiency and reflection coefficient off a gold interface. The experimental reference signal of air, the spectrum when the probe is in contact with water and the normalized SPR fiber optic intensity spectrum are illustrated in Fig. 2(a) and (b).

Theory

The theoretical response of the unmodified fiber optic SPR sensor is illustrated in Fig. 3. In this Figure,

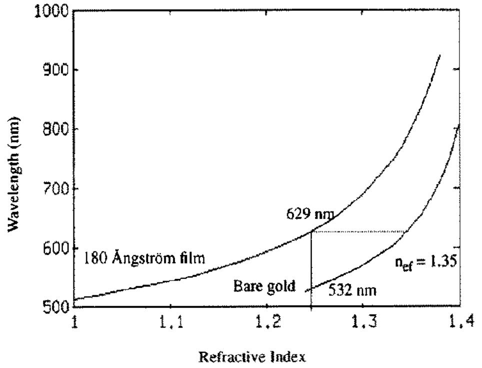

Fig. 3. Plot of the theoretical SPR response curves of a bare gold sensor and one with a 180 Å thick high refractive index overlayer film.

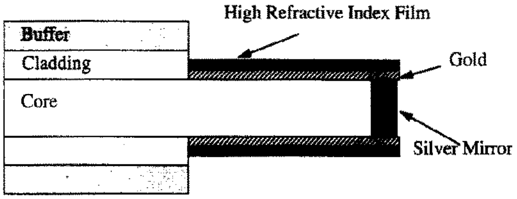

Fig. 4. SPR fiber optic sensor with a high refractive index overlayer film.

the SPR coupling wavelength which is defined as the wavelength of minimum normalized light intensity is plotted versus the refractive index of the sensed medium. The theoretical values were found by calculating the theoretical SPR fiber optic resonance curves using a matrix method to determine the Fresnel reflection coefficients of a multilayered structure and taking into account the allowed propagation angles in the fiber, the energy distribution of the guided modes, and the number of reflections each mode undergoes [7]. The theoretical dynamic range of the sensor is approximately from 1.25 to 1.40 refractive index units. The 1.25 refractive lower limit is due to the fact that the permittivity of gold is too lossy to support SPR at wavelengths lower than 500 nm.

It is possible to extend the dynamic range of the measured refractive index to include lower values by use of high refractive index thin film layers. These films are located at the metal/sensed medium interface of the fiber and symmetrically deposited about the fiber, illustrated in Fig. 4. This method was utilized by Garces *et al.* [8] with a hybrid bulk optic/fiber optic SPR system in which optical fibers were used to transmit light to and from a bulk optic sensor head.

The dynamic range controlling films serves to increase the 'effective refractive index' seen by the surface plasmon wave. This effective refractive index is a function of the film refractive index, film thickness and the bulk refractive index. The SP wavevector is a function of both the film and the bulk dielectric yielding a measured effective refractive index larger than the bulk medium. A bare gold fiber in a 1.25 index of refraction solution yields a resonance near the lower limit of the wavelength region at 532 nm, illustrated in Fig. 3. However, the same sensor with a 180 Å layer of zirconium oxide (refractive index of 2.0) that contacts the same 1.25 index of refraction solution will yield a coupling wavelength of 629 nm.

The theoretical SPR coupling wavelength versus refractive index of the bulk dielectric medium for both the bare gold and zirconium oxide 180 Å film is plotted in Fig. 3. The additional film extends the dynamic range of the sensors from (1.25–1.40) to (1.0–1.40). The measured effective refractive index of the modified probe in a solution of 1.25 refractive index can be graphically determined using Fig. 3. By finding the wavelength at which the modified sensor occurs (629 nm) and holding this wavelength constant, the intersection with the response curve of the bare gold sensor determines the effective refractive index to be 1.35.

The upper refractive index limit of 1.40 is due to the 1000 nm cut off wavelength of a silicon detector. However, even if one was to use a different detector the ultimate refractive index limit would be the refractive index of the optical fiber core, 1.46. This limit is defined by the phase matching condition that insists on the fiber core having a larger refractive index than the sensed medium. Therefore one method in order to extend the upper dynamic range of the sensor involves the use of a fiber core material with a larger refractive index than 1.46.

Experimental methods

A dynamic range controlling film experiment was conducted in which three identical sensors were fabricated with a 9 mm sensor length and a 540 Å gold film. Two of the sensors were then individually mounted in an electron-beam evaporator system and symmetrically deposited with a thin film of zirconium oxide to a thickness of 90 and 180 Å. The three sensors were then individually connected to the SPR fiber optic sensing apparatus and an SPR fiber optic spectrum was measured as each probe was immersed in 11 refractive index standards made of glycerol and deionized water.

An experiment was conducted that used a higher refractive index core in order to increase the upper limit of the refractive index dynamic range of the sensor. A ten inch length of sapphire rod ($n = 1.77$) was acquired that had 1 mm diameter. One end of the fiber was connectorized to a drilled out ST fiber optic connector.

A length of teflon heat shrink was cut so as to cover the entire length of the sapphire rod from the end of the ST connector to within 20 mm of the unconnectorized end of the fiber. A heat gun was used to shrink the tubing around the sapphire rod so as to act like a protective cladding layer. The sapphire fiber was then mounted in the electron beam chamber so as to deposit both the 550 Å thick gold layer about the fiber and the 3000 Å thick silver layer on the end of the fiber. The fiber was then connected to the sensing system. The sensor was then dipped into 18 different refractive index standards (Cargille, NJ, USA) varying in refractive index from 1.4576 to 1.72.

This sapphire SPR sensor was applied towards the monitoring of the curing of an epoxy. The refractive index is known to change during the curing process of an epoxy [9]. Thus, measurement of the refractive index yields information regarding the curing processes of epoxies and composite materials. The refractive index range of epoxies (1.45–1.75) indicated that the sapphire rod based SPR sensor would be the most appropriate sensor to make such measurements. The sensor was introduced into a mix of resin and hardener (5 Minute Epoxy, Devon Corporation, MA, USA). SPR spectra were recorded for the following 30 min.

Results

Results from the dynamic range controlling films are illustrated in Fig. 5. Both the experimental and theoretical data are plotted in the Figure. The SPR coupling wavelengths are plotted versus the refractive index of the standard solutions for all three sensors. The sensor with no film present displayed a dynamic range varying from approximately 1.25 to 1.40 index of refraction units. The sensors with the 90 and 180 Å overlayers of zirconium oxide display the dynamic ranges of 1.15 to 1.40 and 1.00 to 1.375, respectively. There are no experimental data points between 1.00 and 1.33 refractive index due to the limitation of the available chemical samples with refractive indices within this range. The sensitivity to refractive index can be approximated by taking the slope of the response curves and dividing by the SPR coupling wavelength. Assuming the wavelength resolution is 0.25 nm the sensitivity was determined to be between 5×10^{-4} and 5×10^{-5} index of refraction units.

It was not possible to take SPR data for solutions with refractive indices less than water, 1.33. However, it was possible to observe a resonance when the 180 Å zirconium oxide sensor was exposed to air. This result is also plotted in Fig. 5. This finding is very significant, since it allows for the sensors to be applied towards both gas and liquid chemical sensing. The lack of experimental data points within the 1.00 to 1.33 refractive index range does not imply that this range is insignificant. On the contrary, one may observe a response in this region if the 180 Å sensor also had a chemical transducing layer which would cause a shift into this dynamic range. These sensing layers have been employed for gas sensing using traditional bulk optic systems [1, 3].

Figure 6 illustrates the response in the SPR coupling wavelength of the sapphire sensor to the refractive index samples. A dynamic range of refractive index sensing from 1.45 to 1.72 was demonstrated using the sapphire rod sensor configuration. Figure 7 illustrates the measured SPR coupling wavelength versus the time of the epoxy curing process at room temperature. Plotted on the right-hand y axis is the refractive index of the epoxy determined by the SPR coupling wavelength and the calibration curve of Fig. 6.

From this preliminary data it appears that the SPR probe can be utilized in measuring the curing of certain epoxies. Furthermore, it should emphasized that the refractive index of the epoxy placed the coupling wavelength at a relatively non-sensitive portion of the cal-

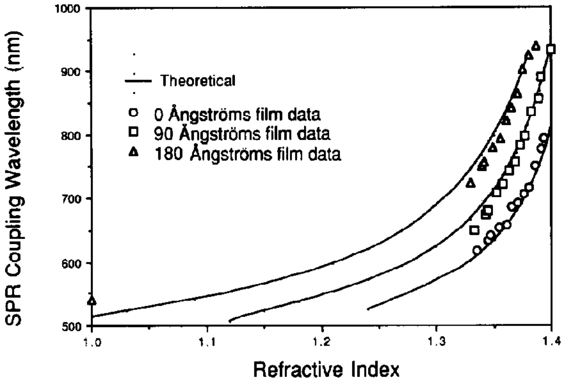

Fig. 5. Experimental and theoretical sensor response to refractive index using dynamic range controlling films.

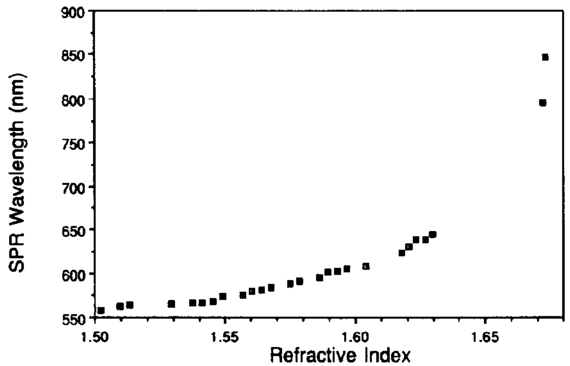

Fig. 6. Experimental sensor response to refractive index using a sapphire based SPR sensor.

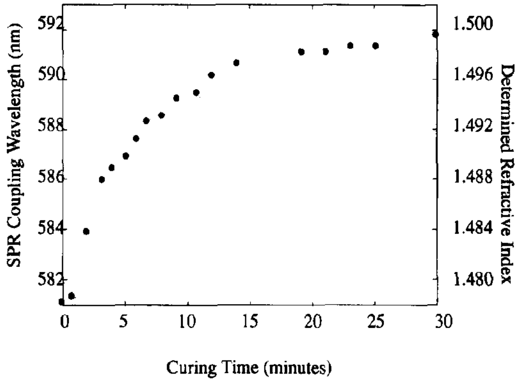

Fig. 7. SPR coupling wavelength shift as a function of epoxy curing time. Plotted on the right-hand side *y* axis is the determined refractive index of the epoxy.

ibration curve of Fig. 6. By using the dynamic range controlling films it should be possible to increase the signal to noise ratio for monitoring this specific epoxy as it cures.

Conclusions

The dynamic range of the fiber optic sensor towards measuring refractive index was shown to be tuned using thin high refractive index overlayers. The maximum dynamic range achieved with the silica based sensor was between 1.0 and 1.375 index of refraction units. This range is significant since it allows for the sensor to be applied towards both gas and liquid chemical sensing. Higher refractive indices up to 1.72 were shown to be sensed using a sapphire core fiber optic sensor. This sapphire sensor was used to monitor the refractive index changes occurring with curing epoxy.

The SPR sensor dynamic range has been shown to be easily adjustable for sensing chemical media with refractive indices between 1.0 and 1.7. This sensor should find utility as a generic platform for the immobilization of selective chemical transducing layers for a variety of chemical sensing applications in the fields of industrial, environmental and biochemical monitoring.

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