Fiber optics based surface plasmon resonance for label-free optical sensing

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With the advancement in the laser technology and availability of low cost optical fibers, there is an increasing trend towards adoption of optical fibers as sensing element for development of optical sensors probes especially point-of-care sensing for environmental, biomedical and clinical application. Refractive index measurement through surface plasmon resonance has evolved to be, one of the most sensitive transducer for label-free sensing with high sensitivity. Surface plasmon resonance is a surface sensitive optoelectronic phenomenon, where light incident on a plasmonic metal surface at a given angle can excite a surface-bound electromagnetic wave, a surface plasmon. Associated with the surface plasmon is an evanescent field that probes local changes in the refractive index of the ambient medium that are used for monitoring analyte- supramolecular/ bio-molecular ligand interactions. Present review outlines a concise view on theoretical aspects of fiber optics based surface plasmon resonance phenomenon and comprehensive updated review on research and development for progression in the design of fiber optics based SPR sensors.

Keywords: Optical fibers, Surface plasmon resonance, FO-SPR sensor, Label-free sensors

1 Introduction

In general, sensors are devices which can sense specific changes in physical properties (physical sensors, e.g., thermometer, barometer, etc.) or chemical properties (chemical sensors like pH electrode, ion selective electrode, etc.) of surrounding environment in real time with high accuracy and precision. Improvisation and inclusion of chemical sensors with biological element (viz; enzyme, antibody, receptors, nucleic acid, whole cell, etc.) having an inherent specificity, combined with sensitivity of advanced transducers and the processing power of modern microelectronics offer novel analytical tool in the form of biosensors. Continuous research and development in this field have resulted in the evolution of third/fourth generation sensors as self-contained integrated devices, capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element. Figure 1 shows schematic of a typical biosensor showing a bio-recognition interface between analyte and transducer. Among the prevailing physico-chemical transducers (viz; optical, electrochemical, thermal, and piezoelectric) used in the development of sensors/biosensors, the optical transducers are the most common, as ample background knowledge about the spectroscopic properties for almost every chemical/biochemical analyte is available.

With the availability of low cost optical fibers and the advancement in laser technology, there is an increasing trend towards adoption of optical fibers as sensing element for development of optical sensors or as a probe. Attention towards use of optical fibers for sensing chemical, biochemical and physical parameters was drawn in 1980s with an approach to provide with a suitable indicator chemistry/biochemistry to the fiber end that responds to the sample in contact; the intensity of reflected, scattered, or reemitted light forms the analytical signal\textsuperscript{1-3}. Evanescent sensing has also been successfully coupled with optical sensing principles, viz., evanescent field absorption, fluorescence, refractive index, and Raman scattering.

Optical fibers have an inherent advantage of being configured for invasive, non-invasive and multiplex analysis; which make them particularly suitable for environmental, biomedical and clinical sensing application. However, one of the challenges in the development of fiber-optic sensor is the high limit of detection and so far the most popular method to overcome this challenge is to utilize fluorescent labels to amplify the signal associated with the presence of the target. However, the disadvantage of fluorescence
is the limited lifetime of fluorescent label and the need to prepare a second labeled target or antibody for detection. Another continuing problem of using fluorescence-based fiber optic biosensors is that of variations in signal response among individual fiber.

Refractive index (RI) measurement through surface plasmon resonance (SPR), offers an attractive alternative optical method for a label-free sensing. SPR is a surface sensitive optical technique for monitoring supramolecular/biomolecular interactions exploiting special electromagnetic waves due to fluctuations in the electron density at the boundary of two materials and till date it represents the most well established transducer for label-free optical biosensing.

Present paper, outlines a concise view on fundamentals of optical fiber, SPR as transducer and a comprehensive review on various configurations of optical fiber core as sensing platform and new opportunities for FO-SPR sensing with the inclusion of nanotechnology. The progression in the design of optical fiber based sensors reveals genesis of label-free sensing from evanescent field wave intensity measurement to RI measurement through SPR, which has evolved in FO-SPR sensor probes that fits in the lab-on-fiber technology.

2 Optical Fibers for Sensing Applications

Optical fiber has a cylindrical core and surrounding cladding both made of silica; the core is generally doped with germanium to make its refractive index \(n_{co}\) higher than that of the cladding refractive index \(n_{cl}\). When a ray of light strikes the boundary interface between these transparent media of different refractive index, the light will be transmitted on the basis of the principle of total internal reflection (TIR). The light propagating through optical fiber consists of two components: the guided field in the core and the exponentially decaying evanescent field decays to almost zero within the cladding. Thus light propagates through the core of the fiber with minimum loss to the surroundings, which was the original object of an optical fiber in propagation of light. However, for sensing applications, light needs to interact with the fiber’s surroundings. One way to achieve this interaction is to expose the evanescent field of the transmitted light. For example, if the cladding of a fiber is reduced or removed, the evanescent field can interact with the surroundings. The distance to which the evanescent field extends beyond the core-cladding interface is called as the penetration depth \(d_p\), which is the distance where the evanescent field decreases to \(1/e\) (0.37) of its value at the core-cladding interface and is mathematically described as:

\[
E(x) = E_0 \exp \left( \frac{-x}{d_p} \right)
\]  

where \(x\) is distance from the fiber core, starting at \(x = 0\) at the core-cladding interface, \(E_0\) is the magnitude of the field at the interface, and \(d_p\) is the penetration depth. The penetration depth is given by:

\[
d_p = \frac{\lambda}{2\pi \sqrt{n_{co}^2 \sin^2 \theta - n_{cl}^2}}
\]

where \(\lambda\) is the wavelength of the light source, \(\theta\) is the angle of incidence of the light at the core/cladding interface, \(n_{co}\) and \(n_{cl}\) are the refractive indices of the core and cladding, respectively.

Typically a single mode optical fiber has a core diameter of 8-12 µm and an overall diameter of ~125 µm and a multimode optical fiber have larger core diameter of 50-200 µm and an overall diameter ranges from 125 to 400 µm and light is propagated along many paths, i.e., multi-mode. In a uniform-diameter single mode fiber, the light only propagates in one mode; however, due to geometry or local RI changes, the single mode fiber becomes multimode, and coupling of modes takes place so that transmission occurs by more than one mode as shown in Fig. 2. In a standard optical fiber, the light propagating through these fibers is insensitive to the surroundings since the
The existence of surface plasmon was first predicted in 1957 by Rufus Ritchie\(^5\) followed by extensive studies in the field of surface plasmon resonance leading to the emergence of SPR as the most versatile sensing principle\(^6-8\). SPR is an optical phenomenon, where the evanescent field wave, instead of interacting directly with the sample, transfers the optical energy to the surface of the metal layer causing coherent oscillation of conduction electrons at a metal-dielectric interface. The quantum of these oscillations is referred to as surface plasmon or surface plasmon wave (SPW). Surface plasmons are accompanied by a transverse magnetic (TM) or p-polarized electric field, which decays exponentially, with maximum at metal-dielectric interface itself. A prism coupling configuration given by Otto and later refined by Kretschmann is generally used to obtain evanescent wave to excite the surface plasmon. For past three decades prism based SPR has occupied top position in sensor technology as transducer for ultrasensitive, specific, label-free and real-time biosensing, especially in biomedical field. Analogous to the prism configuration, a fiber optic configuration by removing the cladding from a small portion of the optical fiber core and coating it with a thin film of metal has been proposed for SPR sensing\(^9,10\).

The visible or IR light beam (~ 500 nm < \(\lambda\) < 1100 nm) under the total internal reflection (TIR) condition can excite surface plasmon; photons are absorbed and transmitted in the media surrounding the sensor, with a precision of the order of \(10^{-7}\). When a light beam incidents through the optical fiber core at an angle greater than the critical angle, at core-cladding interface, the total internal reflection (TIR) of light takes place after penetrating in the lower refractive index medium as evanescent wave. The evanescent wave propagates along the core-cladding interface and decays exponentially in the rarer medium. The evanescent wave can interact with molecules within the penetration depth, thereby producing a net flow of energy across the reflecting surface in the surrounding medium so as to maintain the evanescent field wave and thus resulting in a versatile sensing medium. Since the penetration depth is small in relation to the target analyte, an additional transduction mechanism is employed to amplify the response signal.

### 3 Surface Plasmon and Its Excitation for RI Measurement

The performance of SPR sensors is analyzed with the help of three parameters: sensitivity, signal-to-noise ratio (SNR), and resolution. For the best performance of an SPR sensor, the sensitivity and SNR should be as high as possible. The plasmon SPR parameters are highly sensitive to the dielectric constant of the metal film and the surrounding medium that can be used to detect and study any changes occurring at or near the metal film surface\(^13,14\).
Sensitivity of an SPR sensor utilizing angular interrogation method depends on the amount of shift of the resonance angle with a change in the RI of the sensing layer. For a given RI change if the shift in resonance angle increases this means an increase in the sensitivity of the sensor. Thus the sensitivity ($S_n$) of an SPR sensor utilizing angular interrogation method is defined by the equation:

$$S_n = \frac{\delta \theta_{res}}{\delta n_s}$$  \hspace{1cm} \ldots (4)$$

SNR is a dimensionless parameter strongly dependent on the RI changes. The SNR or detection accuracy of an SPR sensor depends on how accurately and precisely the sensor can detect the resonance angle/ resonance wavelength and hence, the RI of the sensing layer. The narrower the width of the SPR curve, the higher is the detection accuracy. Therefore, if $\delta \theta_{0.5}$ is the angular width of the SPR curve corresponding to reflectance 0.5, the detection accuracy of the sensor is assumed to be inversely proportional to $\delta \theta_{0.5}$. The SNR of the SPR sensor with angular interrogation is, thus, defined by equation:

$$SNR = \frac{\delta \theta_{res}}{\delta \theta_{0.5}}$$  \hspace{1cm} \ldots (5)$$

In SPR sensors with spectral interrogation, the resonance wavelength is determined with reference to the RI of the sensing layer ($n_s$) (i.e., dielectric layer or analyte). If the RI of the sensing layer is altered by $\delta n_s$, the resonance wavelength shifts by $\delta \lambda_{res}$. The sensitivity ($S_n$) can be defined by calculating the shift in resonance wavelength per unit change in refractive index (nm/RIU). Therefore, if $\delta \lambda_{SW}$ is the spectral width of the SPR response curve corresponding to some reference level of transmitted power, the detection accuracy of the sensor can be assumed to be inversely proportional to $\delta \lambda_{SW}$. The SNR of the SPR sensor with spectral interrogation is, thus, defined as Eq. (6), where, $\delta \lambda_{SW}$ can be calculated as the full width at half maximum of the SPR curve (FWHM):

$$SNR(n) = \frac{\delta \lambda_{res}}{\delta \lambda_{SW}} n_s$$  \hspace{1cm} \ldots (6)$$

Resolution ($\Delta n$) of a SPR assay is the minimum amount of change in RI detectable by the sensor. This parameter depends on the spectral resolution ($\delta \lambda_{DR}$) of the spectrophotometer. Thus, for a shift of $\delta \lambda_{res}$ in resonance wavelength, corresponding to a refractive index change of $\delta n_s$, the resolution is given as:

$$\Delta n = \frac{\delta n_s}{\delta \lambda_{res}} \delta \lambda_{DR}$$  \hspace{1cm} \ldots (7)$$

Figure 3(a) shows a plot of reflectance as a function of angle of incidence of the light beam for sensing layer with refractive indices $n_s$ and ($n_s + \delta n_s$). Increase in RI by $\delta n_s$, shifts the resonance angle by $\delta \theta$ and resonance wavelength shifts by $\delta \lambda$; corresponding record of change of RI as resonance unit (milli degree) with time is referred as Sensogram (Fig. 3(b)).

4 Fiber Optics-SPR Sensors: Label-Free Sensing

Introducing SPR in optical fibers sensing system has opened up opportunities for unlimited variations in geometry and composition of sensing layer, resulting in simple and flexible design; miniaturized sensor system; capability of remote sensing for environmental applications and suitability for in-vivo biomedical applications at much lower cost. RI changes induced by molecular interactions are related to the sample concentration or surface density, therefore sensitivity is not dependant on sample size. RI measurements in small volumes have been the key advantage of early label-free sensor/ biosensors for
determination of sugar or protein concentration. Among early fiber optic biosensors, simple configuration proposed by Wolfbeis\textsuperscript{3}, based on measurement of intensity of reflected light. The focus of present review is on progression in design of fiber optics for a label-free sensing (i.e., without secondary amplification) through measurement of EW intensity to RI measurement through SPR. The prism based SPR spectrometry is rarely used outside research laboratories due to bulkiness of the optics involved and high cost of the instrument. In the search of convenient SPR as transducer for sensing technology, the traditional coupling prism-based SPR systems have been replaced by core of an optical fiber, since the propagation of light in an optical fiber is also based on total internal reflection (TIR) as in case of coupling prism. Moreover, the increase in evanescent wave field (EWF) by multi mode transmission and increasing penetration depth ($d_p$) of the evanescent field by tapering or bending the optical fiber; increasing the wavelength and angle of incidence, forms the basis for increased sensitivity of FO-SPR sensor. An updated chronological research and developmental activities in genesis of label-free FO-SPR sensing platform are summarized in Table 1.

4.1 Metal coating at core of optical fiber
First approach of etching of FO cladding to expose core and depositing a thin layer of gold was given by Markatos et al.\textsuperscript{9} Most commonly used metals which support surface plasmon are gold and silver. Gold offers high sensitivity and chemically stable coating for SPR applications whereas silver based SPR sensor offers narrow spectral width, improved accuracy. However, vulnerability of silver to oxidation during application restricts its use in fabrication. Thiol monolayers\textsuperscript{15,16} and chemical coating\textsuperscript{17} has been suggested to protect silver layer from oxidation in FO-SPR sensor and biosensors. A bimetallic layer with silver as inner and gold as outer layer\textsuperscript{18}; multilayer stack of Ag/SiO$_2$/Pd\textsuperscript{19}; ITO coated\textsuperscript{20}; Ag/ITO/Al/ hydrogel layers\textsuperscript{21,22} are some of the options that have been suggested as coating of core of optical fiber. A colloidal gold layer\textsuperscript{23,24} has also been reported for improved SPR parameters. The dynamic range of the sensor can be improved by a single crystal sapphire core fiber\textsuperscript{25}. Apart from gold and silver; copper, titanium and chromium have also been used as metal coating of the core. A multichannel fiber optic sensor on a single-mode fiber by coating silver, gold and copper along with high index titanium oxide on unclad well separated portions of the fiber has been reported by Verma & Gupta\textsuperscript{27}.

4.2 Design of FO-SPR sensor
Early design of Fiber-optics based SPR (FO-SPR) sensor\textsuperscript{10}, involved removal of silicon cladding of optical fiber from a small portion and coated with a metal layer (typically gold and silver) followed by a dielectric sensing layer over it as shown in Fig. 4(a); corresponding sensor setup is shown schematically in Fig. 5(a). This classical approach for construction of FO-SPR has “forward scattering” detection mode, where light enters through one end of optical fiber, propagates through intermediate sensitive zone (where cladding is removed by etching, followed by deposition of a thin ~50 nm Au layer on to the exposed core) and reflected light is received at the other end of optical fiber. The modified portion of FO is immersed in analyte solution and a change in the RI of reflected light is correlated with the sensing of analyte.\textsuperscript{28-32} Esteban et al.\textsuperscript{33} have given a theoretical method to study the surface plasmon excitation in different configurations and metallic layers. A number of studies on FO-SPR have been published in order to achieve better performance parameters\textsuperscript{34-38}. Modeling of FO-SPR sensor for biological investigation\textsuperscript{39} and cross-point analysis of multimode side polished fiber optic sensor have also been reported\textsuperscript{40}.

In spectral interrogation method, the light from a polychromatic source is launched into one of the ends of the optical fiber. The TIR takes place for the rays propagating with an angle in the range varying from the critical angle (depending upon the numerical aperture of the fiber and the light wavelength) to approximately 90°. Consequently, the evanescent field is generated, which excites the surface plasmons at the fiber core-metal layer interface. This coupling of the evanescent field with surface plasmons strongly depends upon light wavelength, fiber parameters, fiber geometry, and metal layer properties. The coupling mechanism is different for single-mode and multimode optical fibers due to mode transmission properties depending upon the number of modes a fiber will support. Further, penetration of the evanescent field and, therefore, strength of light coupling with surface plasmons depends on fiber parameters including, numerical aperture; angle of incidence; length of sensing region and the core diameter of optical fiber. Unlike prism based SPR, the number of reflections for most of the angles is more than one for fiber-based SPR sensor geometry.
Table 1 — Genesis of present state-of-art for fiber optic based label-free sensing platform

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<tr>
<th>Fiber optic sensor: design and assay format</th>
<th>Year of publication</th>
<th>Author ref</th>
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<tr>
<td>Fiber optic sensor based on intensity of reflected light; for measurement of various physical, chemical and biochemical parameters</td>
<td>1987</td>
<td>Wolfbeis(^3)</td>
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<tr>
<td>Optical fiber surface plasmon wave devices by etching the cladding to expose core and depositing a thin layer of gold</td>
<td>1988</td>
<td>Markatos(^9)</td>
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<tr>
<td>Fiber optic sensor based on measurement of optical power; sucrose as test solution</td>
<td>1990</td>
<td>Villuendas and Pelavo(^10)</td>
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<td>SPR based FO sensor with four-layer configuration, improved dynamic range and sensitivity</td>
<td>1992</td>
<td>Garces et al.(^{28})</td>
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<td>Excitation of SPR on the tip of a single-mode fiber; preliminary experiment and theoretical analysis for feasibility of a chemical sensor</td>
<td>1993</td>
<td>Maria et al.(^{29})</td>
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<td>Surface plasmon excitation based “in-line” fiber optic sensor for large range of sensing applications</td>
<td>1993</td>
<td>Alonso et al.(^{30})</td>
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<tr>
<td>SPR based FO sensor for in-situ characterization of multilayered Langmuir-Blodgett films</td>
<td>1993</td>
<td>Mar et al.(^{31})</td>
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<td>FO-SPR probe: multimode optical fiber with Au and Ag modified flat tip, using white light; tested for tetrachloroethane, a classified toxicant and group C possible carcinogen</td>
<td>1993, 1994</td>
<td>Jorgenson and Yee(^{51,52})</td>
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<td>SPR based FO sensor probe with monolayers of polyfluoroalkylsiloxane/ n-alkanethiols over silver coating as dielectric medium; detection of gases and vapors of trichloroethylene, carbon tetrachloride, chloroform, and methylene</td>
<td>1996, 1997</td>
<td>Abdelghani et al.(^{15,16})</td>
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<tr>
<td>SPR based multimode FO sensor probe with polymeric sensing layer ; monochromatic excitation; for chemical sensing in liquid and gas phase, resolution 10(^{-4}) RIU</td>
<td>1996</td>
<td>Trouillet et al.(^{53})</td>
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<tr>
<td>SPR based side-polished single-mode FO sensor, Resolution 10(^{-4}) RIU</td>
<td>1998</td>
<td>Slavík et al.(^{54})</td>
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<td>SPR based single-mode FO sensor probe coated with thin gold film; tip polished at an angle relative to the longitudinal axis; resolution 10(^{-5}) RIU</td>
<td>2001, 2002</td>
<td>Slavík et al.(^{62,63})</td>
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<td>SPR based plastic optical fibers (POFs) sensors and devices</td>
<td>2000</td>
<td>Bartlett et al.(^{86})</td>
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<td>SPR based FO sensor with zirconium acetate covered silver coating; chemical and biological sensing with improved sensitivity</td>
<td>2001</td>
<td>Lin et al.(^{17})</td>
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<td>SPR based tapered FO sensor for on-line monitoring</td>
<td>2001</td>
<td>Díez et al.(^{64})</td>
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<td>Theoretical approach for SP excitation in different configurations of optical fiber</td>
<td>2002</td>
<td>Esteban et al.(^{33})</td>
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<td>SPR based FO sensor with an inverted Graded-Index profile; RI detection range 1.33 to 1.39</td>
<td>2002</td>
<td>Bardin et al.(^{34})</td>
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<td>SPR based multimode FO sensor with thin palladium layer over metal coating; detection of hydrogen at 0.8% with response time of 300 s.</td>
<td>2002</td>
<td>Bévenot et al.(^{35})</td>
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<td>SPR based wavelength modulation FO sensor based on single-mode polarization maintaining fiber (PMF); robust design for field conditions, RI detection as low as 4\times10^{-6}</td>
<td>2003</td>
<td>Piliarik et al.(^{41})</td>
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<td>SPR based FO dip-probes: robust design</td>
<td>2004</td>
<td>Obando et al.(^{65})</td>
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<td>SPR based FO microsensor: tapered end coated with nano gold; employing white-light; RI in the range of 2\times10^{-4}</td>
<td>2004</td>
<td>Grunwald &amp; Holst(^{100})</td>
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<td>SPR based FO exploiting LSPR of gold nanoparticles adsorbed at end face of optical fiber; affinity bio sensor resolution of 10(^{-5}) RIU</td>
<td>2004</td>
<td>Mitsui et al.(^{96})</td>
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<td>SPR based FO sensor with asymmetric metal coating on a uniform waist single-mode tapered fiber; improved dynamic range</td>
<td>2004</td>
<td>Hernández et al.(^{39})</td>
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<tr>
<td>SPR based D-type FO sensor with heterodyne interferometry; based on phase-difference variations, sensitivity upto 2\times10^{-6} RI units; suitable for in-vivo testing</td>
<td>2005</td>
<td>Chiu et al.(^{42})</td>
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<td>SPR based D-type FO sensor with a thin gold film; theoretical analysis</td>
<td>2005</td>
<td>Wang et al.(^{44})</td>
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<td>SPR based tapered FO sensor; suitable for vapour and liquid phase samples</td>
<td>2005</td>
<td>Kim et al.(^{67})</td>
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<td>SPR based FO sensor with single crystal sapphire for in-situ monitoring</td>
<td>2005</td>
<td>Kim et al.(^{25})</td>
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<td>SPR based FO sensor with ITO coating; physico-chemical studies</td>
<td>2005</td>
<td>Konry &amp; Marks(^{20})</td>
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<td>Microfluidic FO waveguide for RI based sensor based on Micro-Opto-Electro-Mechanical Systems (MOEMS); for biosensing applications</td>
<td>2005</td>
<td>Chandrasekaran &amp; Packirisamy[^102]</td>
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<td>SPR based FO sensor with variation in metallic layer coating: bimetallic layers, nano gold films and Ag-Au alloy nanoparticle films</td>
<td>2005</td>
<td>Sharma &amp; Gupta[^18]</td>
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<td>SPR based FO sensor with nano particle films Ag-Au alloy: effect of LSPR</td>
<td>2006</td>
<td>Sharma and Gupta[^14]</td>
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<td>SPR based D-type FO sensor; theoretical model based on the Kretschmann's configuration and heterodyne interferometry by numerical simulation</td>
<td>2006</td>
<td>Wang et al.[^43]</td>
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<tr>
<td>SPR based single-mode tapered FO sensor: RI sensing by multiple-peak SPR</td>
<td>2006</td>
<td>Hernández &amp; Villatoro[^68]</td>
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<td>Surface plasmon-polariton based FO sensor with Bragg grating; simulations on the coupled-mode method at telecommunication wavelengths</td>
<td>2006</td>
<td>Nemova &amp; Kashyap[^74]</td>
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<tr>
<td>Surface plasmon-polariton based hollow core FO sensor with Bragg grating; theoretical model</td>
<td>2006</td>
<td>Nemova &amp; Kashyap[^75]</td>
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<td>Surface plasmon-polariton (SPP) FO sensor with Bragg grating long-range waveguides; theoretical performance of structures comprising a thin metal film of finite width embedded in a homogeneous background dielectric</td>
<td>2006</td>
<td>Charbonneau &amp; Berini[^78]</td>
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<td>SPR based FO nanosensor with nano size tip coated with ~ 40 nm gold; surface plasmon wave excited near the tip to achieve high sensitivity</td>
<td>2006</td>
<td>Chang et al.[^101]</td>
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<td>SPR based FO sensor with metal coating of Au, Ag, Cu and Al: characterisation of sensors parameters</td>
<td>2006</td>
<td>Mitsushio et al.[^26]</td>
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<td>SPR based FO sensor with optimized microfluidics; RI changes of 10^-4 RIU leads to detection of 1% change in the transmitted light intensity</td>
<td>2006</td>
<td>Hassani &amp; Skorobogaty[103]</td>
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<td>SPR based plastic FO sensor with lateral bends as sensitive area; multipoint liquid-level measurement sensor</td>
<td>2007</td>
<td>Lomer et al.[^83]</td>
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<td>Evanescent field based tapered FO probe; designed for SPR phase matching</td>
<td>2008</td>
<td>Yu et al.[^70]</td>
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<td>SPR based tapered FO sensor: performance profile of different taper configurations: linear, parabolic, exponential-linear</td>
<td>2008</td>
<td>Verma et al.[^49]</td>
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<td>SPR based U-shape FO sensor doped with self assembled gold Nps; resolution ~ 10^-3 RIU for chemical sensing; femtosecond laser micromachining for fabrication</td>
<td>2010</td>
<td>Chen et al.[^107]</td>
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<td>SPR based FO sensor with multilayer stack of Ag/SiO2/Pd as sensing layer; spectral modulation instead of on intensity modulation, hydrogen sensing</td>
<td>2011</td>
<td>Perrotton et al.[^19]</td>
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<td>RI measurement with plastic fiber optic realized in Poly (methyl methacrylate core coated with gold thin films; suitable for liquids with RI ~1.35</td>
<td>2011</td>
<td>Cennamo et al.[^84]</td>
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<td>SPR based plastic fiber optic sensors: comparison of performance with silica based optical fiber</td>
<td>2013</td>
<td>Cennamo et al.[^85]</td>
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<td>SPR based FO sensor with Ag/ITO/Al/hydrogel coating; pH sensing. Thermal evaporation coating for metals and dip-coating of hydrogel, (3-acrylamidopropyl)-trimethylammonium chloride</td>
<td>2013</td>
<td>Mishra &amp; Gupta[^21]</td>
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<td>SPR-Based FO sensors with Au-Ag alloy nanoparticles coating; effect of alloy composition and particle size on sensitivity</td>
<td>2013</td>
<td>Tu et al.[^115]</td>
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<td>SPR based multimode FO with metallic nanohole arrays: Next generation FO-based plasmonic sensors</td>
<td>2013, 2014</td>
<td>Jia &amp; Yang[^105,106]</td>
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<td>SPR based FO sensor with Ag/ITO/Al/hydrogel coating; detection of CrO_4^{2-} in aqueous samples</td>
<td>2014</td>
<td>Mishra &amp; Gupta[^22]</td>
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<td>2014</td>
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<td>SPR based multi channel FO sensor probe: A single fiber, three probe coated with silver, gold and copper along with high index titanium oxide on unclad well separated portions of the fiber, tested with sucrose solution</td>
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The number of reflections directly affects the SPR curve width, therefore, performance parameters (SNR and sensitivity) of the sensor. An optical fiber SPR sensor based on polarization-maintaining fibers and wavelength modulation is presented by Piliarik et al.\textsuperscript{41}. It is demonstrated that this design provides superior immunity to deformation of optical fibers of the sensor and, thus allows for more accurate SPR measurements under realistic operation conditions and could resolve RI changes as low as $4 \times 10^{-6}$ under moderate fiber deformations. The numerical aperture, relates to the light acceptance limit of the fiber. Designs include side-polished U-shaped and D-type\textsuperscript{42-44} fiber optic for SPR sensing. Among tapered geometries...
prevalent for biochemical sensing, fiber optic can be nonadiabatic (NATFO) with small taper angle (light propagating in fundamental mode) or adiabatic with higher taper angle, as in biconical taper optic fiber (BTOF) allowing coupling of light modes. The Non-adiabatic optic fiber sensors are essentially RI sensors, whereas an adiabatic tapered fiber has been used for RI measurement in SPR format. Tapered fiber optic (TFO) structures have also been adapted in forward scattering mode of SPR as in biconical tapered fiber and uniform core radius sandwiched between two tapered fiber region have constituted useful alternatives to enhance the performance of FO-SPR sensors for the past many years. From the early nineties, Jorgenson and Yee have reported the first FO-SPR probe, where the cladding around the tip of a multimode optical fiber was dissolved, a thin Au film (~55 nm) around the circular side of etched tip was deposited by electron-beam evaporation, followed by deposition of thin silver sheet (~300 nm) on the flat end fiber optic distal tip. Since then number of studies has been published towards miniaturization of fiber optic surface plasmon resonance sensor using this simple flat type fiber optic tip design for label-free chemical sensing and biosensing including monitoring DNA hybridization and DNA-protein interactions with improved sensitivity.

The flat tip of FO probe replaced by a tapered tip fiber optics (TFO) shows a substantial variation in evanescent field penetration along the tapered sensing region whereas an untapered fiber exhibits uniform penetration of the evanescent field along the sensing region. Slavik et al. have reported a single-mode FO with one end polished at an angle relative to the longitudinal axis and coated with a thin gold film for SPR sensing. TFO structures are the most versatile configuration which can adapt “backward scattering” detection mode for much improved performance parameters, less susceptible to stress-induced break and more suitable for in-situ sensing in varied sample environment. Although tapered tip probe configuration in FO biosensor has been extensively used in fluorescence label based FO sensors, however with the inclusion of nanotechnology in FO-SPR design to amplify the signals, TFO probes with localized surface plasmon resonance (LSPR) are emerging as popular sensing tools.

4.3 FO-SPR dip-probes

The classical approach of “forward scattering” detection mode suffered difficulty in localized etching/dissolution of cladding, making the optical fiber susceptible to stress-induced breaking. Another approach for fabrication of optical fiber sensor follows “backward scattering” detection mode, involve de-cladding at one end of optical fiber, followed by deposition of thin metallic layer (Au or Ag) as shown in Fig. 4(b) can truly be called as FO-SPR probes, corresponding sensor setup is shown schematically in Fig. 5(b). FO-SPR probe is immersed in the analyte solution, where the light propagates as well as reflected back at the distal end of optical fiber.

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4.4 Fiber grating structures for SPR sensing

The fiber grating structures represents the most widely studied technology to support optical fiber for chemical and biochemical sensing for increased sensitivity by detecting change in the RI of surrounding solutions. In grating configuration, the sensor generates a “comb-like” spectrum of SPR resonances, due to individual coupling of the core mode light to a multitude of cladding modes, providing a mechanism to eliminate the background effect due to cross reactivity. Under phase matching conditions, a Bragg grating (FBG) couples the forward propagating core mode to
the backward propagating core mode; a long-period fiber grating (LPG) can couple the forward propagating core mode to one or a few of the forward propagating cladding modes; and tilted fiber grating (TFG) can couple the forward propagating core mode to the backward propagating core mode and a backward propagating cladding mode. FBG structures is inscribed inside the core of a single-mode FO using the phase-mask technique, where FO is exposed to intense ultraviolet (UV) laser light through a grooved glass plate, before covering the cladding by a thin Au film (~50 nm). FBGs are most widely used as fiber optic sensor heads. A notable step in the progress of fiber optic based label-free was proposed by introducing Bragg grating into the core of optic fiber. The advantages of Bragg grating technology is associated with its intrinsic wavelength multiplexing ability, whereas LPG present high sensitivity to RI measurement but cross sensitivity to others parameters can be a limitation.

Pennington et al. have demonstrated the detection of large molecules (proteins) and small molecules (pesticides) biosensor based on LPG technology. The LPG sensor is a spectral loss optical fiber based system that provides direct detection of large molecules, by using an antigen or antibody modified hydrogel, without the need for secondary amplification. The binding of the specific target results in a mass increase that produces a localized refractive index change around the LPG region and thus a spectral shift in the observed wavelength loss band. Charbonneau and Berini have studied theoretical performance of Bragg gratings based on long-range surface plasmon-polariton waveguides. Novel label-free sensor fabrication strategy with Fabry-Pérot type distributed Bragg gratings for FO based dielectric waveguide biosensor has been reported by Kehl & coworkers which in contrast to single Bragg grating reflector, exhibits an extended measurement range as well as relaxed fabrication with standard lithographic means and is independent of expensive light-sources and/or detectors, making an affordable but sensitive device, potentially suitable for point-of-care applications.

Caucheteur and co-workers have proposed several label-free configuration in fiber optic sensor including laser-induced eccentric Bragg grating and photo-induced tilted gratings into the core of the fiber for biosensing applications. The sensor architecture lies on gold-coated tilted fiber Bragg gratings (Au-coated TFBGs) photo-imprinted in the fiber core via a laser technique. TFBGs operate in the near-infrared wavelength range at ~1550 nm, yielding optical and SPR sensing characteristics that are advantageous for the analyses of cellular bindings and technical compatibility with relatively low-cost telecommunication-grade measurement devices. A leap in this direction is ability to detect an acoustic wave with a resolution of $10^8$ RIU employing a gold-coated highly tilted Bragg grating that excites a spectral comb of narrow band-cladding modes with effective indices near 1.0 and below. Further, a molecularly imprinted conductive polymer is synthesized around the cylindrical surface of a gold-coated optical fiber following an electro-polymerization process, where the metal film is used as a working electrode during the procedure in order to make the polymer grow on top of it. In addition, the fiber core is previously photo-inscribed with a tilted fiber Bragg grating to benefit from its surrounding refractive index sensitivity. It is believed that these configurations may open research directions for highly sensitive plasmonic sensing in gas.

4.5 Composition of optical fiber for SPR sensing

Apart from silica glass, plastic optical fibers (POFs) have also been proposed for SPR sensing. Plastic optic-fibers are especially advantageous due to their low cost, excellent flexibility, easy manipulation, great numerical aperture, large diameter, and the fact that plastic is able to withstand smaller bend radii than glass. The classic geometries of silica based fiber optic have been adopted in POF where devices are based on the excitation of surface plasmons at the interface of test medium and a thin gold layer deposited on a photosensitive buffer spin coated on the plastic fiber core or directly on the fiber core. The configuration with the photosensitive buffer layer exhibits better performance in terms of detectable refractive index range and signal-to-noise ratio.

Fiber optics based infrared sensing has been long established technique as fiber evanescent wave spectroscopy (FEWS) for efficient, non-destructive and selective detection of organic and biological species. This technique combines the benefits of ATR spectroscopy with the flexibility of using a fiber as the transmission line of the optical signal, which allows for remote analysis during field measurements or in clinical environments. Silica based glass prism or optical fiber based SPR measurements restricts the sensors to operate in the visible light range. Plasmon parameters of excitation in the IR range have lead to advantageous properties in SPR sensing. SPR
excitation with IR-light involves the use of advanced materials like silicon prism\textsuperscript{90,91} and chalcogenide glass prism\textsuperscript{92,93} as coupling material in Kretschmann configuration. Chalcogenide glasses\textsuperscript{94,95} have also been used to fabricate fiber optics sensor using evanescent wave spectroscopy employing IR light. Red light emitting diode (LED) as a light source and localized SPR of gold nanoparticles adsorbed at end face of optical fiber, have shown sensitivity comparable to the conventional prism SPR biosensors\textsuperscript{96}.

The performance of FO-SPR sensors widely depends on the adhesion of the gold layer to the FO silica core, thereby often representing a major limiting factor in achieving the properties of the benchmark SPR systems. In this direction recent report of Arghiret \textit{et al.}\textsuperscript{97} has brought in significant advancements in coupling surface plasmon resonance to optical fiber technology describing fabrication protocol for silanized optical fiber wherein 3-marcaptopropyl trimethoxysilane (MPTMS) acts as adhesion promoter for developing robust and reusable Au surfaces on the three-dimensional FO-SPR sensing probe. A complete optical sensor system based on POF-SPR platform integrated into a thermo-stabilized flow cell has been proposed for biochemical sensing\textsuperscript{98,99}.

5 FO-SPR Sensing Opportunities with Nanotechnology

Nanotechnology has influenced SPR based fiber optic sensor technology to a great extent. FO-SPR sensor configurations offers lower sensitivities with relatively modest LODs in comparison to the conventional prism based SPR devices. Nano coating of Au, silica and/or magnetic nanoparticles (NPs) have amplified the SPR response, thereby improving the performance parameters. Two important recently explored research areas offering advantages small dimensions, high sensitivity to RI, and possibility of multiplex sensing are: micro-interferometers based on micro/nano-structured fibers and nanostructures doped fiber optic probes.

5.1 Micro/nano-structured optical fibers

During last decade, much effort has been focused on miniaturizing fiber-optic SPR sensors. A single-ended tapered nano gold coated fiber-optic microsensor has been reported to probe the affinity between analyte and biological molecules in real time, without label, with a resolution in the range $10^{-4}$ RI units employing white light\textsuperscript{100}. A sensitive nano-optical fiber biosensor fabricated by shaping a fiber tip to taper under 100 nm size, wherein a 3-D coded finite-difference time-domain approach verifies the excitation of the surface plasmon wave and the differences among its intensities has been measured in media of various refractive indices\textsuperscript{101}. Incorporation of micro structured optical fiber (MOF) into a biochip for evanescent-wave-sensing where the fiber-optic waveguides based Micro-Opto-Electro-Mechanical Systems (MOEMS) form a significant class of biosensors with notable advantages, viz., light weight, low cost and ability to be integrated with biosystems\textsuperscript{96}. Fiber-based SPR sensors with optimized microfluidics are also proposed, where, plasmons on the inner surface of large metalized channels containing analyte can be excited by a fundamental mode of a single-mode micro structured fiber\textsuperscript{102,103}, wherein the fiber-optic waveguide is integrated with micro-machined fluidic channel across which different chemical and biological samples are passed through. The nano patterning of FO-SPR surfaces using lithographic techniques is among the latest development in nanotechnology, paving the way toward high-performance LSPR sensing. Although reports on nano patterning of optical fibers tips with arrays of metallic nanostructures came in the beginning of this century\textsuperscript{104} however, their application in designing high performance FO-SPR based real-time biosensing has been reported recently by Jia and Yang\textsuperscript{105,106} as the next generation FO plasmonic sensors, offering tremendous possibilities for miniaturization, multiplexing and/or small molecules detection in low concentrations.

5.2 Nano-functionalized FO-SPR probes

Localized surface plasmon resonance (LSPR) in optical fiber sensors has proved to be a crucial advancement FO-SPR sensing platforms. LSPRs are collective electron charge oscillations in metallic nanoparticles that are excited by light. They exhibit enhanced near-field amplitude at the resonance wavelength; the field is highly localized at the nanoparticles and decays rapidly away from the nanoparticles/dielectric interface into the dielectric background, though far-field scattering by the particle is also enhanced by resonance. Light intensity enhancement by LSPRs and very high spatial resolution limited by the size of nanoparticles has attracted various groups\textsuperscript{107,108} for immobilization of nano material onto the FO-SPR probes. Gold nanoparticles\textsuperscript{109,110} and metal alloys nanoparticles\textsuperscript{114,115} coating onto the FO-SPR probes provides an increased surface area for molecular
recognition based immunoassay as well as increased perturbation of the evanescent field, generating strong LSPR effects. The immobilization of Au nanoparticles involves pre-silanization of the optical fiber tip using (3-mercaptop propyl) tri-methoxysilane (MPTMS) or 3-aminopropylmethoxysilane (APMES), prior to attaching the chemically synthesized gold nanoparticles\textsuperscript{110,111}. Shao \textit{et al.}\textsuperscript{112} have reported gold nanoparticle assembled film built on the polyelectrolyte (PE) multilayer modified sidewall of an unclad optical fiber as the sensing layer for constructing an optical fiber localized surface plasmon resonance (LSPR) biosensor. Renoirrt \textit{et al.}\textsuperscript{116} have used silver wires (1–3 $\mu$m $\times$ 0.04–0.05 $\mu$m) synthesized by a polyol process to immobilize onto a single mode optical fiber with the Langmuir–Blodgett technique. The advantage of the nanowire approach is to provide a much increased contact surface area for molecular recognition-based sensing. Another class of fiber-optic SPR sensor exploits the localized SPR of self-assembled gold colloids which are on the grating portion of a long-period fiber grating\textsuperscript{23, 24}. Lin \textit{et al.}\textsuperscript{117} have developed a side-polished multimode fiber sensor with a ∼37 nm gold thin film (by dc sputtering), until half the core is closed and coated; the measurement system using the halogen light source has been used for several SPR based real-time detections. Use of graphene as a replacement for conventional metal films\textsuperscript{118} in FOBS for biochemical sensor application and a nanocomposite film of poly -methyl methacrylate /reduced graphene oxide deposited over copper film\textsuperscript{119} onto the unclad portion of the optical fiber have also been reported for construction of ammonia gas sensor.

Depositing metallic nanoparticles onto the tip of a cleaved optical fiber has realized into a dip sensor probes\textsuperscript{120,121}, where light coupled into the fiber interacts with the localized surface plasmons within the nanoparticles at the tip; a portion of the scattered light re-couples into the optical fiber and is analyzed by a spectrometer. Characterization of the sensor demonstrates an inverse relationship between the sensitivity and the number of particles deposited onto the surface, with smaller quantities leading to greater sensitivity. The results obtained showed that by depositing nanoparticles with distinct localized surface plasmon resonance signatures with limited overlap, as for the case of gold and silver nanospheres, a multiplexed dip biosensor can be realized by simply functionalizing the different nanoparticles with different antibodies after the fashion of an immunoassay. In this way different localized surface plasmons resonance bands responsive to different target analytes can be separately monitored, as further presented below, requiring a minimal quantity of reagents both for the functionalization process and for the sample analysis. Saigusa \textit{et al.}\textsuperscript{122} have suggested electrosprun nano fibers of poly (vinylidene fluoride) (PVDF) with gold nanoparticles as substrate for future label- free sensing applications. Ultrathin metallic nanofilms have recently gained substantial attention in plasmonics. Niobium nanofilms (∼10 nm thickness) has been proposed recently\textsuperscript{123} as an alternate to gold coating towards achieving low-loss hybrid plasmonic modes.

6 Conclusions

The development of optical-fiber sensors during recent years is related to two of the most important scientific advances of the 1960s, the laser and modern low-cost optical fibers. During the late 1980s optical fibers were used in the development of the biosensors with fluorescent probe and since then their application has continued to progress in clinical, biomedical, environmental, industrial and military applications. At the same time refractive index measurement through surface plasmon resonance has evolved to be, one of the most sensitive transducer for label-free and real-time monitoring of bimolecular interactions. Exploitation of optical fiber platform for SPR measurement have turned out in the development fiber-optic-SPR sensors as low cost, compact, lightweight, minimally invasive product which can be multiplexed effectively on a single fiber network. The fact that all supramolecules based ligands and biomolecules have refractive properties, and that SPR detects refractive index changes close to the surface, no labeling is required. There is an unlimited scope in research and development for fiber-optics based SPR sensor in environmental, biomedical and clinical field where real-time, label-free and cost effective sensing are the key factors for point-of-care monitoring. This review includes theoretical aspects of fiber optics based SPR phenomenon and a comprehensive account of the progress in research and development of FO-SPR probes that fits in the lab-on-fiber technology.

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