



Semiconductor metal oxide/polymer based fiber optic lossy mode resonance sensors: A contemporary study

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ABSTRACT

Lossy mode resonance (LMR) based sensors have gained attention in the literature during last two decades. Understanding lossy nature of the optical modes guided through the optical substrates took researcher's interest to their applications in the field of diagnostic and sensing of various analytes. In this review, the attention has been paid to the emergence and developments of LMR phenomenon as a fiber optic sensing platform. Concept and basic configuration of LMR sensor and parameters evaluating the performance of such sensors have been discussed in detail. Optical materials such as transparent semiconductor metal oxides (TSMOs) and few polymers have been found to support LMR. In view of this, optical fiber based chemical and biosensors utilizing such materials have been reviewed. In addition, the analysis of the potentials of LMR based bulk/nanostructured sensors with future possibilities have been discussed.

1. Introduction

The relevance of sensors in preserving chemical environment safety and biomedical science advancement is quite known in present day. The sensor application overreaches areas of agriculture, water-air-food quality control, drug delivery, surgical-clinical diagnostics and remote control. Accurate and quick detection, stability and reproducibility, good shelf life, cost effectiveness, easy handling, compactness and portability are the features needed to be met by the modern sensing schemes for real time applications. Among the sensing transducer mechanisms established for practical applications and purposes, optical scheme of target analyte detection using optical fiber is significant because of its electromagnetic immunity, isolation to electrical parameter variations, ruggedness, multiple and point of care detection feasibilities, real time monitoring and remote analysis practicalities [1].

In any field, the role of sensor depends on the mechanism on which sensor works. This mechanism is dependent on the materials used for the sensor probe fabrication and the chemistry of reactions between the target analyte and these materials to confirm the existence of the analyte. In an optical transducer incorporated sensor system, the substrate can be prism/glass, grating, waveguide or fiber. Optical fiber, having core, cladding and buffer jacket as the composition layers, can be designed suitably in a sensor model by removing unwanted layers (buffer, cladding) and by attaching additional transducing material's layer for the probe realization. The techniques used to realize an optical sensor

for chemical and biological applications are many in number, such as luminescence, absorption, scattering, diffraction, fluorescence, resonances imparted by thin films/nanostructures of metal and dielectrics (metal oxides, polymeric layers) and so on [2]. Of these, a combination of optical fiber as substrate and thin film/nanostructures as technique accomplishing resonance/sensing layer is mostly opted by researchers. Such systems make use of opto-chemical/opto-biological correlative properties of materials to realize direct or indirect detection of chemical/bio-analytes [3,4].

A major segment in the materials category utilized for realizing chemical and biosensors implemented on optical substrates (prism/waveguide/fiber) are metals and transparent semiconductor metal oxides (TSMO) [5,6]. Of these, literature shows works reported in a large number using metals such as silver, gold, aluminium, etc. for realizing a sensor. The plasmonic behaviour of the metals in the visible region of electromagnetic spectrum, supports their realization as a transducing layer in sensor probe fabrication by implementing surface plasmon resonance (SPR) phenomenon [7–10]. Lots of reports and reviews came up in literature demonstrating the usage of metal thin film exhibited surface plasmon resonance and metal nanostructure exhibited localized surface plasmon resonance (LSPR) [8,11–13].

At the same time, the highly conducting TSMOs exhibit more feasibilities than metals in optical sensor field. This is due to their catalytic behaviour, wide band gap which supports tunable conductivity along with high transparency in visible region, cost effectiveness, dielectric

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nature, reversible interactions, and surface, structural and electronic properties [14,15]. The capability of TSMO to act as dielectric/lossy material in the visible region as well as a plasmonic material in the infrared region opened a major scope in sensor technology. Consequently, optical sensors for chemical and biological analyte detection have been realized making use of the resonance caused by the lossy nature of TSMO in the visible region [16]. The phenomenon of resonance realized using the lossy behaviour of TSMOs over unclad fiber or any other optical substrate is termed as lossy mode resonance (LMR). When light propagating through the fiber incidents at the semi-conducting metal oxide clad-core interface, the mobility of the charge carriers (electron and holes) in the semiconducting metal oxide changes. This, in turn, changes the conductivity of the lossy material which is related to its permittivity as

$$\varepsilon_m = \varepsilon_r + i\varepsilon_i = \varepsilon_r + i \frac{\sigma}{\omega\varepsilon_0} \quad (1)$$

where ε_m is the material permittivity with real part ε_r and imaginary part ε_i , σ is the material conductivity, ε_0 is the material permittivity in vacuum and ω is the frequency. Thus, a change in conductivity changes the permittivity which in terms of refractive index can be expressed as

$$\varepsilon_m = (n_m)^2 = (n + ik)^2 \quad (2)$$

Hence, the real and imaginary parts of refractive index change with the change in the permittivity. The refractive index of the semiconductor material is wavelength dependent. In optical concept, the modes guiding through the core of the optical fiber becomes lossy in the region of fiber with semiconducting metal oxide cladding. In such a region, the rearrangement of modes takes place and a resonance condition occurs. The resonance characteristic depends upon the optical properties such as dielectric constant/refractive index of the semiconducting metal oxide and the medium surrounding it.

Generally, in a chemical or biosensor, the sensing layer interacts with the target analyte. The interaction changes the properties of the material layer (optical, electrical, mechanical) which is detected and analysed by the transducer. A correlation of optical and chemi/bio-sensing concepts, works in an optical based chemical/biosensor in such a way that the chemical and biochemical reactions happening at the material-analyte interface changes the material optical properties such as refractive index. The sensor monitors the change in the refractive index, to calibrate the changes in the analytic behaviour. A change in the refractive index changes the wavelength at which the resonance condition is satisfied. A measurement of the resonance condition can be taken as the evaluation factor to track the analyte characteristics. This is the basic idea used for implementing LMR based optical sensors using TSMO. Although the field of LMR based sensors is still in its infant stage, since last six years the field has started evolving considerably. The field explores possible materials supporting the phenomenon along with its application in optical sensing of chemical and biological analytes [17,18]. Various TSMOs such as zinc oxide (ZnO), indium tin oxide (ITO), indium oxide (In₂O₃), tin oxide (SnO₂), titanium oxide (TiO₂) and few polymers have been reported in the literature to support lossy mode resonance [19]. These high index materials based LMR sensors have very high sensitivity, label free sensing, short response time and fast recovery [20,21]. The technique, in this way, competes with the existing optical techniques such as scattering, absorption, metal enhanced fluorescence, SPR and LSPR in optical sensing performance [19,22,23].

Therefore, this recently developed field/method of sensing needs more attention. Due to this requirement, the present review article concentrates on lossy mode resonance based sensors. It begins with the design and developments of optical LMR sensors. A detailed discussion on conditions of a material to generate LMR, the performance parameters of LMR based sensors and TSMO materials that exhibit LMR are included. This is followed by a brief description on LMR exhibited by the other general TSMOs. Further, the review covers the TSMO material

wise optical sensing applications reported so far for chemical and biological analyte detection with real time evaluation and online monitoring schemes. A concluding remark on the further developments possible in the field to enhance the performance and scope in commercializing the sensors are discussed.

2. Implementation of LMR in optical sensors

The phenomenon of lossy mode was first recognized by Marciniak et al. in 1993 by realizing the propagation of electric field from the guided dielectric substrate to the over layer made of semiconductor (cladding medium) at a cut-off thickness [24]. The guided modes that leaks from the substrate to the semiconductor cladding is termed as the leaky modes or lossy modes [16]. The coupling of such modes with the guided modes results in a resonance phenomenon, named as lossy mode resonance (LMR). The implementation of LMR in sensing is pioneered by Andreev et al. in 2005 [25]. As mentioned above, LMR is sensitive to the refractive index of the external medium. Since, the refractive index is a function of the wavelength of the light, a change in the external refractive index changes the wavelength generating resonance. The wavelength at which LMR occurs is called as the resonance wavelength while the resonance phenomenon exhibited was given the name as index sensitive mode resonance [25]. In the work reported by Andreev et al., the material used for realizing LMR was silicon, which was coated over unclad single mode optical fiber. In 2008, the study was further extended by the same group to enhance the refractive index sensitivity by replacing silicon with ZnO, a TSMO [26]. The work studied the possibility of its application in sensing using index sensitive mode resonance exhibited by TSMO material for the first time. In 2010, Villar et al. showed another TSMO, indium tin oxide (ITO), as a transduction layer for sensor realization, confirming its importance in sensing applications [27]. Since then around seventy papers for sensing applications utilizing LMR realized on optical fibers have been reported in the literature. The field addresses a new concept of utilizing the technique for enhanced performance in the desired wavelength range of electromagnetic spectrum. Hence, to explore the further possibilities and advances that can be made in the field, it is necessary to understand the concept and configuration for realizing the LMR phenomenon.

2.1. Concept and configuration

Consider the propagation of light through a substrate having dielectric constant $\varepsilon_1 = \varepsilon_{r1} + i\varepsilon_{i1}$, without any significant loss. If we consider any TSMO with dielectric constant $\varepsilon_2 = \varepsilon_{r2} + i\varepsilon_{i2}$ over the substrate, then the properties of light propagating through the substrate change. This is due to the interaction of light with TSMO at the TSMO/substrate interface. As discussed in the introduction section, the mobility of charge carriers and hence the conductivity of the TSMO is dependent on the wavelength of the interacting light [16]. In such an arrangement, the change in conductivity causes a fraction of light to tunnel from substrate to TSMO. This fraction of light guiding through the TSMO is generally referred as lossy since it is the part of light that got lost from the guided substrate mode. These propagating modes are termed as the lossy modes. In fact, the phenomenon is the rearrangement of the guided modes at the substrate-TSMO interface while the propagation of light occurs, which is termed as LMR [19]. As a lossy mode propagates through the TSMO, the propagation vector of light guiding through the TSMO changes. This happens due to the arise of lossy nature of the guided mode, which increases the imaginary part of its dielectric constant. An increase in imaginary part causes more amount of light to get absorbed by the TSMO. Thus, a decrement in the transmitted power measured at the output end of the substrate occurs and is depicted as a dip in the transmitted spectrum. The wavelength corresponding to dip is called as the resonance wavelength. The essential condition for LMR realization is that the real part of the dielectric constant of TSMO should be positive and higher in magnitude

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