EVANESCENT WAVE FIBRE OPTIC SENSORS: DESIGN, FABRICATION AND CHARACTERIZATION

Thesis submitted
in partial fulfilment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

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MAY 2000

To my loving parents

DECLARATION

Certified that the work presented in this thesis is based on the original work done by me under the guidance of Dr. P Radhakrishnan, Professor, International School of Photonics, Cochin University of Science & Technology and has not been included in any other thesis submitted previously for the award of any degree.

Cochin-22
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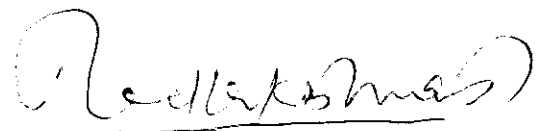
CERTIFICATE

Certified that the research work presented in this thesis is based on the original work done by Mr. Shelly John M under my guidance in the International School of Photonics, Cochin University of Science & Technology and has not been included in any other thesis submitted previously for the award of any degree.



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PREFACE

Although guided waves in an optical fibre have potential use in telecommunication, their utilisation for sensing applications has become promising and hence fibre optic sensing has turned out to be an emerging field in photonics technology. Measurement of various physical and chemical variables, including pressure, temperature, magnetic field, current, rotation, acceleration, displacement, chemical concentration, reaction rate, pH, detection of pollutant gases etc. have been achieved using fibre optic sensors. Several meritorious features as well as attractive capabilities of fibre optic sensors have brought them to the forefront of other sensing methods. They offer immunity to electromagnetic interference, radio frequency interference and geometrical versatility. Since optical fibres are purely dielectric, it can be used in hazardous areas where conventional electrical or electronic sensors are not safe. Fibre optic sensors have added advantages like very short response time and remote-sensing capability, which mean that transmission of information from various sensor heads to the destination, could be easily achieved.

A variety of schemes including different modulation techniques have been adopted in the design and development of fibre optic sensors. Among these modulation schemes, intensity modulated fibre optic sensors are much more simple and inexpensive without pledging the sensitivity. The present thesis discusses the design, fabrication and characterization of some intensity modulated optical fibre sensors based on the evanescent wave in the cladding region of a multimode fibre.

The thesis is organised into five chapters. The contents of the each chapter are outlined below.

Chapter 1 gives a general but brief introduction to Fibre Optic Sensors. This deals with the classification of fibre optic sensors and different modulation aspects of fibre based sensing techniques. This chapter discusses the various ongoing research and development activities in this frontier field all around the world. It reviews different

optical fibre based sensor design, methods and applications. Without much discussion about the basic theory behind each sensor development, the picture will not become clear and perfect.

Chapter 2 deals with evanescent wave theory and it also discusses the attenuated total internal reflection at the core–cladding interface and theoretical understanding of the evanescent field based fibre optic sensors. When light propagates in an optical fibre or wave-guide a fraction of the radiation extends to a short distance from the guiding region into the medium of lower refractive index that surrounds it. This evanescent field decays exponentially with distance from the wave-guide interface. This evanescent tail of the light propagating in the rarer medium is utilised for the development of various sensors. There are a lot of advantages like enhanced sensitivity, possibility of miniaturisation, capability to use in on-line measurements etc for the evanescent wave fibre optic sensors. Also no coupling optics is required in the sensor region for these sensors. These inherent merits are the motivating factors in the development of evanescent wave sensors. An awareness of the critical parameters that determine the extent of evanescent wave interactions is important for the optimal design of evanescent wave sensor. This chapter also deals with the theoretical background necessary for the optimisation of the sensor region.

In **Chapter 3,** we have introduced a novel method for the deposition rate measurement of thin films using optical fibre sensors. This technique overcomes most of the demerits of the conventional methods for the deposition rate measurement. A comparative analysis of the different conventional techniques is given in this chapter along with the relative merits and demerits of the new method. The characterization of this fibre optic evanescent wave sensor is carried out in the case of silver thin films produced by pulsed laser deposition. Also, the fibre optic sensor has been successfully employed for the deposition rate measurement of aluminium thin films produced by thermal evaporation method. With proper calibration, the sensor can be used to measure thickness of thin films as well. It offers much more advantages than a quartz crystal

monitor, which widely used for thickness monitoring. This fibre optic sensor is found to be highly sensitive and can also be used for remote sensing.

Sensing chemical variables and monitoring chemical processes are important aspects of chemical technology. Development of optical fibre based chemical sensors is one of the promising areas of research. **Chapter 4** deals with the design and development aspects of a fibre optic sensor to measure glucose concentration. This sensor works on the principle of evanescent wave absorption phenomena. The fibre optic sensor system has been found to be very sensitive at low levels of glucose concentration with saturation at about 4 gm/litre. Compared to other methods, this fibre optic sensor is simple, inexpensive and works in a direct manner. This chapter also gives detailed description of the fabrication techniques of a hand held optical fibre based device for the measurement of glucose concentration. The system can be easily adapted to measure glucose concentration in urine.

Chapter 5 is devoted to the design and characterization of an evanescent wave fibre optic sensor to detect toxic gases. Sensitive detection of the pollutant gases like nitrogen dioxide, ammonia and methane etc. is found essential in industrial applications, environment pollution monitoring and in mines. This chapter discusses a novel approach for the detection of NO_2 utilising the evanescent waves in a multimode plastic clad silica fibre by replacing a portion of the cladding with organic materials such as metalphthalocyanines and rare earth phthalocyanines. A comparative study of these phthalocyanine coated fibre sensors as well as the reusability of the sensor is also included in this chapter.

SOME OF THE RESULTS OBTAINED WERE PUBLISHED:

a) Papers Published in Journals

1. 'A fibre optic evanescent wave sensor for monitoring the rate of pulsed laser deposition of metal thin films', **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, *Meas. Sci. Technol.* Vol. 10, No.2, pp N17-N20, 1999.

2. 'An optical fibre based evanescent wave sensor to monitor the deposition rate of thin films', Deepa Jose, **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, *Thin Solid Films*, Vol. 325, pp264-267, 1998.

3. 'A voltage sensor using polarization maintaining fibre', **M Shelly John**, P Radhakrishnan, V P N Nampoori, C P G Vallabhan, S Binu and M Ramachandran, *J of Optics*, Vol. 26, No. 2, pp 95-98, 1997.

4. 'A force sensor using polarization maintaining fibre' **M Shelly John**, S Binu, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, *Commun. in Instrum.*, Vol.6, No. 1, January-March 1998.

5. 'A fibre optic sensor to measure glucose concentration' **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, *Commun. in Instrum.*Vol. 6, No. 1, pp 107-112, April-June, 1998.

6. 'Fibre optic evanescent wave sensor to monitor the rate of deposition of aluminium thin films', **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, *Optics and Optoelectroincs-Theory, Devices and Applications*, Edited by O P Nijhawan, A K Gupta, A K Musla and Kehar Singh, Narosa Publishing House (New Delhi), Vol. 1, pp 421-423, 1998.

7. 'Monitoring the rate of pulsed laser deposition of silver thin films using a fibre optic sensor', **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, Photonics-98, *International Conference on Fibre Optics and Photonics*, Edited by Anurag Sharma and Ajoy Ghatak, Viva Books Pvt. Ltd. (New Delhi), Vol. 3, pp 1033-1036, 1998.

b) Papers presented at conferences

1. 'Evanescent wave sensor to measure glucose concentration', **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, Proc. of the International Conference on Fibre Optics and Photonics, PHOTONICS-96, Tata Mc-Graw Hill (New Delhi),pp 367-368, 1997.

2. 'Evanescent wave sensor to monitor the rate of deposition of thin films' Deepa Jose, **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, International Conference on Micro-Optics Integration and Assemblies, part of SPIE's Optoelectronics and High-Power Lasers & Applications, San Jose, CA (1998).

3. A fibre optic sensor to measure absorbance', **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, Proc. of National Laser Symposium, BARC (Bombay), pp C29-30, 1996.

4. 'AC voltage sensor using polarization maintaining fibre', **M Shelly John**, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, Proc. of National Laser Symposium, CAT (Indore), pp 159-160, 1997.

5. 'A PC based fibre optic sensor for the on-line measurement of pH', N Salim, H Nizamudhin, C V Dally, **M Shelly John** and P Radhakrishnan, Proc. APSYM-98, National Symposium on Antennas and Propagation (CUSAT, Cochin), p 181, 1998.

6. 'NO_2 detection with a fibre optic evanescent wave sensor', **M Shelly John**, J Thomas, K P Unnikrishnan, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, International Symposium on Photonics and Applications (ISPA-99), held during 29 November – 3 December, 1999 at Singapore (Oral presentation).

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SHELLY JOHN M

CONTENTS

Chapter 4

GLUCOSE CONCENTRATION MEASUREMENT USING FIBRE OPTIC SENSOR

Chapter 5

EVANESCENT WAVE FIBRE OPTIC SENSOR TO DETECT NITROGEN DIOXIDE

Chapter 1

INTRODUCTION TO FIBRE OPTIC SENSORS

Abstract

This introductory chapter gives delineation about different types of fibre optic sensing systems. An overview of the different modulation mechanisms adopted for the design and development of fibre sensors are also dealt with in this section. We have discussed the major merits of these optical fibre based transducers over conventional sensing techniques. In this chapter we have mainly emphasised on intensity modulation schemes especially sensing devices dependant on evanescent waves.

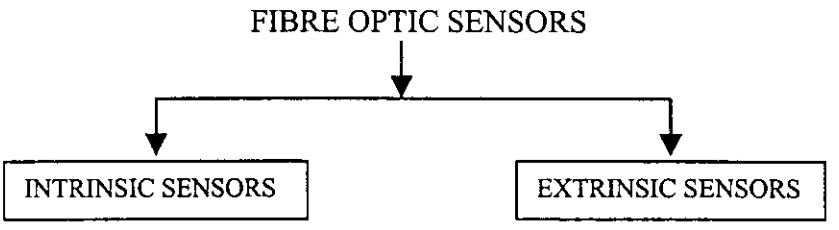
1.1 Introduction:

The technological advancement of Photonics is very rapid compared to other technologies. Now-a-days we can find that its involvement in other potential technologies has grown enormously. The broad spectrum of applications of photonic devices gives us an illustration of the importance of this emerging field. We can see the incorporation of different types of lasers, dielectric waveguide structures and photodetectors that cover from ultraviolet to far infrared for the fundamental research as well as for a variety of applications.

Optical fibres have a major role not only in communication but also in the development of different types of sensors. These fibre optic sensors (FOS) form a lion's share of contribution to the photonics technology as a whole[1-4]. Fibre optic sensing is facilitated by its salient features, which make it prominent among other sensing methods. These fibre optic sensors successfully meet the requirements like high sensitivity and quick response in sensing different chemical and physical variables. Using optical fibre sensing devices one can measure or monitor different physical and chemical parameters in terms of one of the principal parameters that describes the light

beam[5-12]. These principal parameters include light intensity, phase, polarisation and wavelength. The characteristic features and promising capabilities of fibre optic sensors make them attractive and place them in the forefront of the Photonics technology. In the fibre optic sensing system, the sensed signal is immune to electromagnetic interference (EMI) and radio frequency interference (RFI). Since optical fibres offer low loss to the signal propagating through it we can use this method for remote sensing applications[13]. In this case we place the control electronics for sources and detectors far away from the sensor head. Another meritorious capability is its high flexibility and as a point sensor they can be used to sense normally inaccessible regions without perturbing the transmitted signals. One of the attractions of fibre optic sensors is their multiplexing capability to large number of individual sensors in a fibre network[1]. We can see numerous other advantages like chemical inertness, intrinsically safe operation in explosive environments and potentially resistant nature to nuclear or ionising radiations. Another notable feature of fibre optic sensors is their low volume and weight and hence they are very much convenient to use. These optical fibre based sensors offer electrical insulation and can be used for detection of high voltage and current[14-17]. Moreover, FOSs are highly reliable and secure with no risk of fire or spark.

In fibre optic sensors (FOSs) the light may be modulated either inside or outside the fibre and hence we can broadly classify them as intrinsic sensors and extrinsic sensors.



In intrinsic sensors, the physical parameter or effect to be sensed modulates the transmission properties of the sensing fibre. Here one of the physical properties of the guided light like intensity, phase, polarisation, etc. is modulated by the measurand. In

extrinsic type fibre sensors the modulation takes place outside the fibre. In this case the fibre merely acts as a conduit to transport light signal to and from the sensor head.

Based on the modulation technique, fibre optic sensors can be classified into 5 different groups.

1. Intensity modulated fibre optic sensors
2. Phase modulated fibre optic sensors
3. Polarisation modulated fibre optic sensors
4. Frequency modulated fibre optic sensors
5. Wavelength modulated fibre optic sensors

Among these modulation techniques, the first three modulation schemes are most commonly employed in a wide range of applications.

1.2 Intensity modulated fibre optic sensors:

Among the above mentioned fibre optic sensing schemes, intensity modulation is the simplest and the cheapest way of detecting or measuring different parameters. In intensity modulated fibre optic sensors, the measurand modulates the intensity of the transmitted light through the fibre and these variations in intensity is measured using a detector situated at the output end of the fibre. These fibre optic sensors offer the easiest method of implementation and compatible with the multimode fibre technology. The intensity modulation can be achieved in a variety of methods[2,3].

Intensity modulation can take place through light interruption due to the displacement of one fibre relative to another or misalignment of one fibre with respect to other fibre. This misalignment can take place in three different ways, which are axial (longitudinal) misalignment, transverse misalignment and angular misalignment. Among these three methods, transverse misalignment fibre sensor is more sensitive. Sensitivity of such fibre optic sensors can be enhanced by cleaving and polishing the two ends at a slant angle and keeping the slant face of the two fibres sufficiently close.

Due to frustrated total internal reflection power will leak from the first fibre to the receiving fibre through slant face[2].

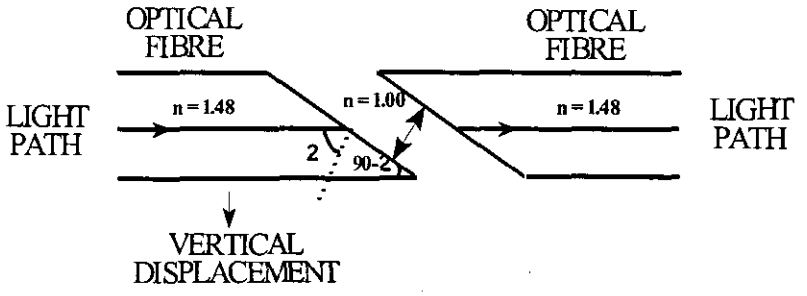


Figure 1.1 Figure showing the frustrated total internal reflection.

In another class of intensity modulated fibre optic sensors the measurand modulates the light reflected from a reflecting surface. A Y coupler fibre consisting of two multimode fibres cemented somewhere along their length forms a reflective fibre optic sensor probe. Two bundles of fibres or two fibres fused along their length can form the reflective fibre probe. The working of this intensity modulated fibre sensor is as shown in figure1.2.

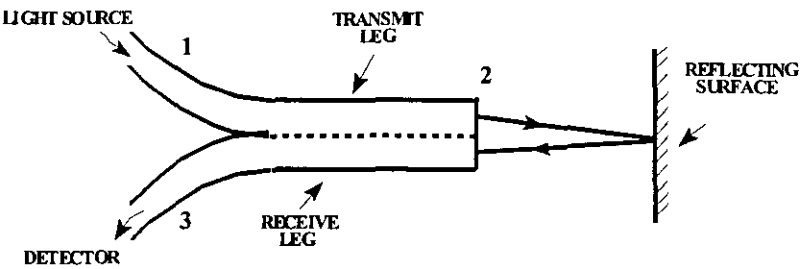


Figure 1.2 Reflective fibre optic sensor

Light is injected through port 1. The intensity of the back reflected light that will exit through port 3 would depend on the distance of the reflecting target from the fibre probe. These reflective fibre sensors can be used to measure displacement, pressure etc. The main applications of these types of sensors are in medical catheters as inter-cardiac

pressure transducer and in fibre laser doppler anemometry. These Y coupler fibre probes have been used to determine surface texture, flow of pulp suspension in a tube etc.

A certain class of intensity modulated fibre optic sensors are working on the basis of transmission loss occurring due to microbending of the optical fibre[2]. This technique is widely utilised for the measurement of acoustic pressure, strain, temperature, displacement etc. Here the fibre may be sandwiched between a pair of toothed or serrated plates to induce microbending as shown in figures 1.3 and 1.4.

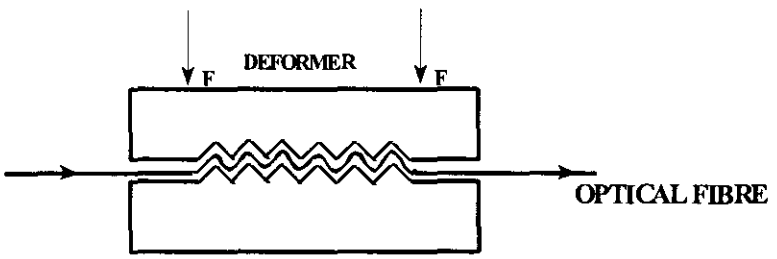


Figure 1.3 Microbending in an optical fibre

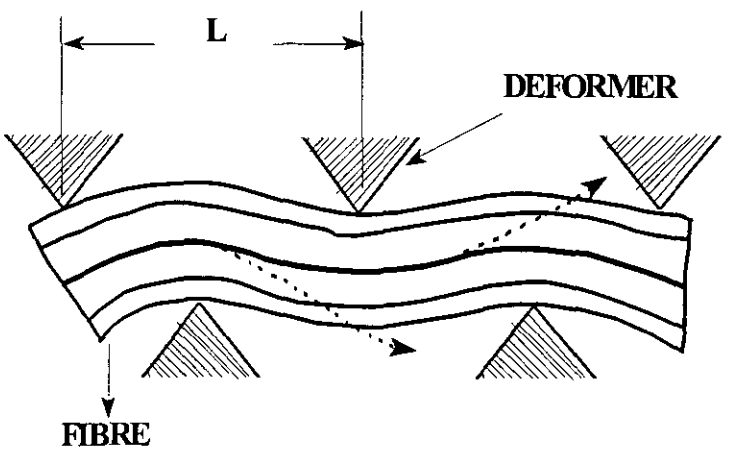


Figure 1.4 Principle of microbending in an optical fibre

This brings about redistribution of guided power between modes of the fibre and also coupling of power from one mode to another. If the spatial wavelength (Λ) of periodic deformation satisfies the phase matching condition $\beta_p - \beta_q = \frac{2\pi}{\Lambda}$, power transfer will take place from p-th to q-th mode. β_p and β_q represent the modal propagation constants of two modes. If q-th mode is the radiation mode, this power transfer will result in a net transmission loss of the guided modes. The critical spatial wavelength Λ_{cr} of a deformer required to induce transfer of power from the highest order guided mode to radiation modes in the case of a step index fibre will be

$$\Lambda_{cr} = \frac{\pi a}{\sqrt{\Delta}} = \frac{\sqrt{2}\pi a n_1}{NA}$$

where 'a'- core radius, Δ - core-cladding index difference, n_1 – core index, NA – numerical aperture.

The microbend induced loss in a multimode fibre is given by $\alpha = \frac{K a^4}{\Delta^3 b^6}$

where 'b'- cladding radius, K – proportionality constant. Thus by monitoring the decrease in intensity of light guided through the fibre core, we can construct a pressure or displacement sensor.

In the case of graded index fibre, adjacent guided modes are seperated from each other by a constant difference in wavenumber space $\Delta\beta = \frac{\sqrt{2\Delta}}{a}$

The spatial wavelength of the deformer, required to couple power between adjacent modes is given by

$$\Lambda = \frac{2\pi}{\Delta\beta} = \frac{2\pi a n_1}{N A}$$

If W is the optical power at fibre input and T represents the transmission coefficient of the fibre, the power received by the detector will be WT. If P represents the change in pressure applied to the deformer, this will lead to an effective force ΔF on the microbend fibre causing the amplitude X of the bent fibre to change by ΔX.

The transmission coefficient of the fibre will change by ΔT as

$\Delta T = (\Delta T/\Delta X)\, D.\, \Delta P$,

where $D.\, \Delta P = \Delta X$ and D – a constant that depends on the pressure change

$\Delta T = \left(\frac{\Delta T}{\Delta X}\right) A_p k_f^{-1} \Delta P$ - for pressure. Similarly we can obtain the change in transmission coefficient for various environments as

$\Delta T = \left(\frac{\Delta T}{\Delta X}\right) \alpha_s\, l_s\, \Delta\theta$ - for temperature

$= \left(\frac{\Delta T}{\Delta X}\right) m_p\, k_f^{-1}\, \Delta a$ - for acceleration

$= \left(\frac{\Delta T}{\Delta X}\right) d_{33}^{H}\, l_s\, \Delta H_F$ - for magnetic field

$= \left(\frac{\Delta T}{\Delta X}\right) d_{33}^{E}\, l_s\, \Delta E_F$ - for electric field

where A_p, m_p are area and mass of deformer plates respectively, α_s and l_s are thermal expansion coefficient and length of the spacers. d_{33}^{H} - represents the magnetostrictive strain coefficient of the spacer material in the magnetic field H_F. d_{33}^{E} is the piezo electric strain constant in the electric field E_F. k_f – the bent fibre force constant and is given by

$$k_f = \frac{3\pi Y d^4 N}{\Lambda^3}$$

where Y is the Young's modulus, d – diameter of the fibre, N – number of bent intervals.

Thus we can measure or detect a variety of physical variables using this type of intensity modulated fibre optic sensing technique.

Apart from the above-mentioned intensity modulation mechanisms, there are other schemes to achieve intensity modulation in fibre optic sensors for the detection or measurement of different physical and chemical variables. In certain fibre optic sensors a shutter will be actuated by the measurand resulting in the interruption of optical beam between two opposed fibres. This principle can be employed for the construction of

optical fibre microswitch devices that can be used to detect displacement, pressure or acoustic waves. Fibre optic refractometers are an effective tool for the measurement of refractive index of liquids through intensity modulation of light.

1.2.1 Evanescent wave fibre optic sensors:

Evanescent wave technique is one of the sensing methods used in a certain class of fibre optic sensors for monitoring and measurement of a variety of physical and chemical variables[21-28]. These are intensity modulated sensors and the present thesis discusses the design and development of FOSs based on evanescent fields. An evanescent field is created whenever light undergoes total internal reflection at the boundary between two dielectric media. The evanescent field penetrating into the cladding decays exponentially (Figure 1.5).

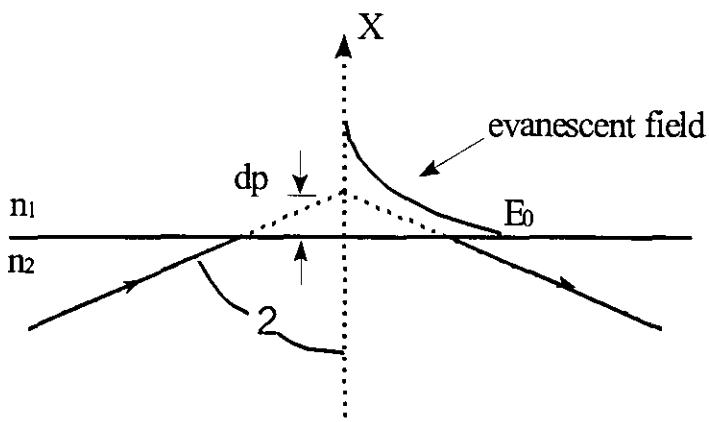


Figure 1.5 Evanescent waves in the lower index region

Utilising this exponentially decaying portion of the guided waves, a variety of sensing devices have been designed and developed. But the disadvantage of this type of sensor is that the sensitivity is dependent on the mode distribution and hence on launching conditions and external disturbances.

When considering the absorption of evanescent wave, the evanescent power that can interact with the analyte is a critical parameter. This quantity is closely related to the fraction 'r' of the total guided power that resides in the cladding region[29].

$r = P_{clad}/P_{total}$

V parameter of the optical fibre has an important role in this context. Substantial values (>50%) for 'r' can be achieved in single mode fibres. Even though high sensitivity is achievable with single mode fibres, there a lot of practical difficulties in incorporating them in different sensor designs. The two possible configurations for using them are as shown in figure 1.6.

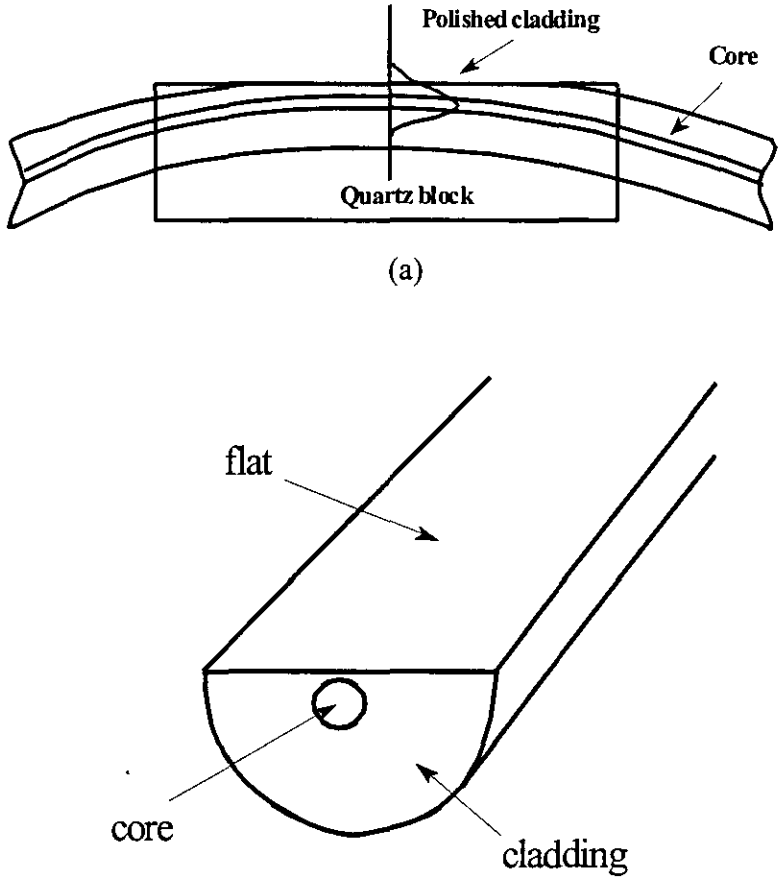


Figure 1.6 Evanescent wave sensor designs with single mode fibres

(a) Polished fibre block

(b) D-fibre

In the first case the single mode fibre is first mounted in a curved slot cut in a quartz block and the top surface is polished to remove the cladding region on one side of the fibre. There are a lot of disadvantages for this system. Only a very short length of the fibre is exposed to evanescent field. Also, it is time consuming to fabricate this design. In the second design, the fibre is made from a conventional preform with half of the cladding region removed. So the fibres pulled from the preform have a D-shaped cross-section, allowing continuous access to the evanescent field along the whole length of the fibre. Again, the disadvantages are the limited commercial availability of D-fibres and problems associated with splicing and connecting these fibres into systems.[3]

Even though the fraction of the total guided power available in the cladding region of a multimode fibre is limited, they offer higher guided power throughput and better coupling efficiency.

1.3 Phase modulated fibre optic sensors:

The most sensitive fibre optic sensing method is based on the optical phase modulation. The total phase of the light along an optical fibre depends on the properties like the physical length of the fibre, transverse geometrical dimension of the guide, refractive index and the index profile of the waveguide. If we assume that index profile remains constant with environmental variations, then the depth of phase modulation depends on the other remaining parameters. The total physical length of an optical fibre may be modulated by the perturbations like thermal expansion, application of longitudinal strain and application of a hydrostatic pressure causing expansion via Poisson's ratio. The refractive index varies with temperature, pressure and longitudinal strain via photo elastic effect. Waveguide dimensions vary with radial strain in a pressure field, longitudinal strain in a pressure field and by thermal expansion. The phase change occurring in an optical fibre is detected using optical fibre interferometric techniques that convert phase modulation into intensity modulation[1,2,18]. There are a variety of fibre optic interferometers like Mach-Zehnder, Michelson, Sagnac and Fabry-Perot as shown in figure 1.7.

Optical fibre interferometric sensors have applications in areas like industries, military and scientific measurements.

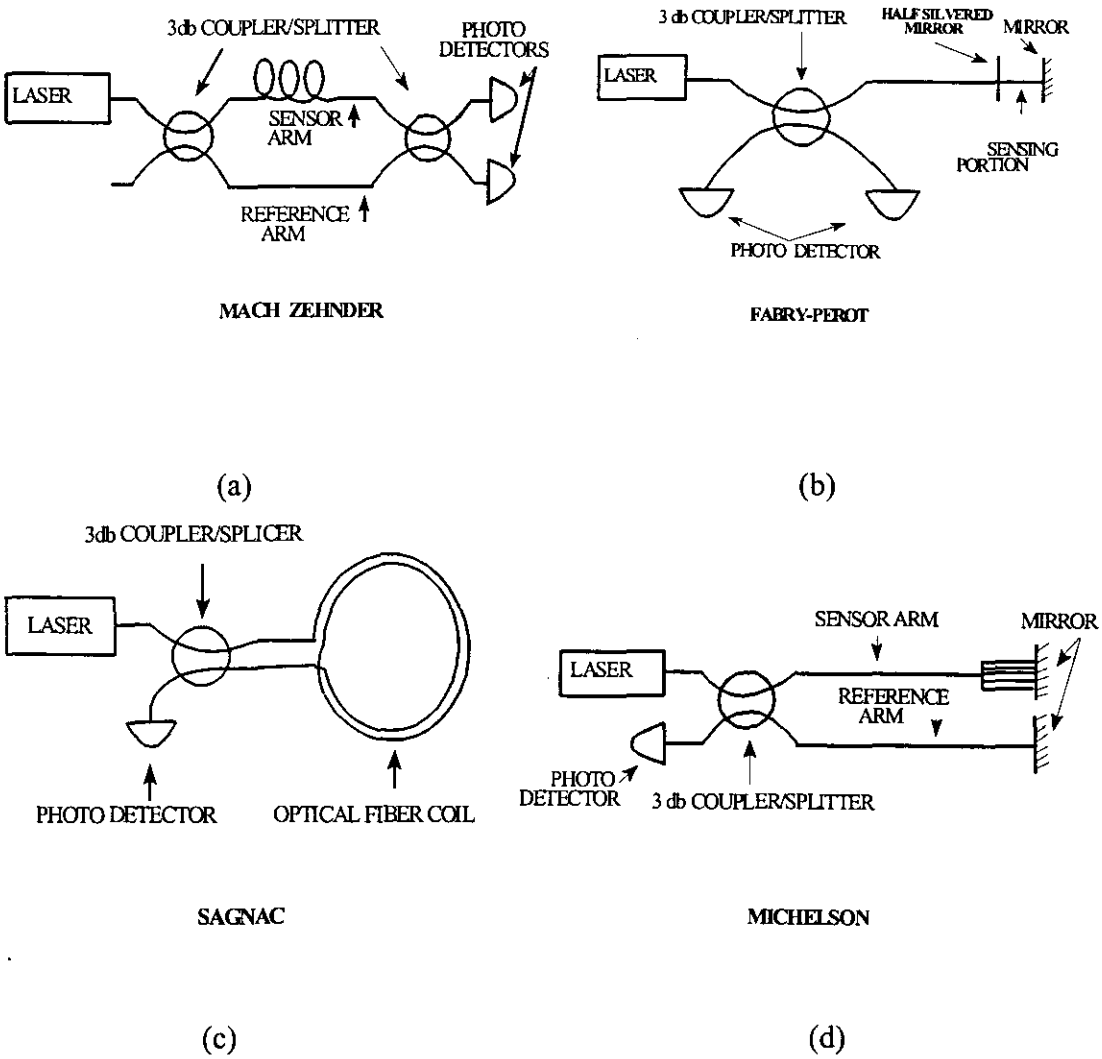


Figure 1.7 Optical fibre interferometric sensors
(a) Mach Zender (b) Fabry-Perot (c) Sagnac (d) Michelson

As conventional interferometers are very much sensitive to external disturbances, they are generally not suitable for applications outside the research laboratory. But the use of fibre optic interferometric sensors avoids most of the obstructions rendered by the former techniques and can greatly extend the range of applications.

1.4 Polarisation modulated fibre optic sensors:

Polarisation properties of optical fibres are important for a certain class of sensors. This property can be easily modified by many external variables and hence polarisation modulated fibre optic sensors can be used for the measurement of a range of parameters. Special fibres and other components have been devised with specific polarisation features and these are widely used in a variety of measurement applications as well as in communication and in signal processing.

The action of any given external field on the polarisation properties of an optical fibre is normally to modify either the linear or the circular birefringence component.[1,2,4] Thus the measurand modulates the state of polarisation (SOP) in a fibre polarimetric sensor. A variety of physical phenomena influence the state of polarisation of light and hence introduce birefringence. Some of them are Optical activity, Faraday rotation, Electrogyration, Electro-optic effect, Kerr effect, Photoelastic effect etc. A variety of physical parameters can be detected and measured using these phenomena.

1.5 Optical fibre chemical sensors:

A chemical sensor is a device that can be used to measure the concentration or activity of a chemical species in a sample.[9] The qualities like chemical inertness, low weight and small volume of optical fibres along with advantages like immunity to electromagnetic interference and easy availability have promoted the research and developmental activities in the area of fibre optic chemical sensors (FOCSs)[9-11,28,30]. Hence these optical transduction allows a wide variety of chemical detection schemes that were previously impossible using conventional potentiometric and amperometric electro-chemical devices. FOCSs have high potential to make rapid and selective in-situ measurements of a specific chemical species.

The most commonly found fibre optic chemical sensor (FOCS) designs are,

1. Distal-type probes in which the indicator is immobilised at the tip of a bifurcated fibre optic bundle or single optical fibre.
2. 2. Evanescent field type

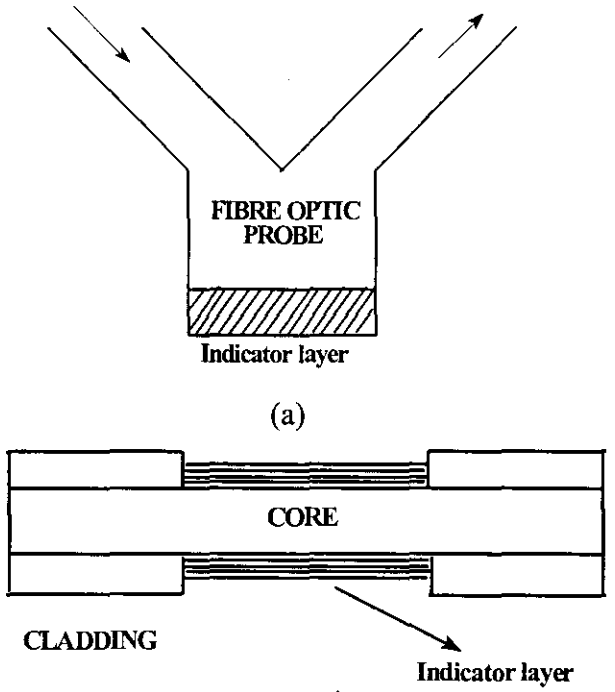


Figure 1.5 Two common fibre optic chemical sensor designs.
(a) Distal type probes
(b) Evanescent wave type

1.5.1 Ion sensing:

FOCSs for the detection of ions like hydrogen have been the subject of major research. The simplest example of an ion selective FOCS is a fibre optic pH sensor with a fluorescent pH indicator dye immobilized at the distal end of a fibre optic probe. For the detection of aluminium (III) ions, morin is immobilized. Reaction between these two species generates a highly fluorescent complex that can be monitored by simple fluorescence measurement.

1.5.2 Gas sensing:

Two techniques, fluorescence quenching and acid – base chemistry, have been used for a variety of gas sensing FOCS designs. FOCS for oxygen detection is based on fluorescence quenching of an immobilized fluorophore ($Ru(Phen)_3^{2+}$) that is trapped in or positioned behind a gas permeable barrier.

Simple acid-base chemistry can be used to build FOCSs for acidic and basic gases such as ammonia, carbon dioxide, hydrogen cyanide and nitrogen dioxide. A gas permeable membrane separates the sample from a layer that contains the pH indicator dye. The acidic or basic gas crosses a membrane, enters the indicator layer and undergoes a proton transfer reaction with the dye. The extent of this reaction is monitored spectroscopically through a fibre optic probe.[9]

1.5.3 Non-gaseous molecules:

The simplest design for the detection and quantification of a non-gaseous molecular species is based on direct spectroscopic detection. Here fibre optic probes are used to guide the light to a distant sampling site and then to transmit the resulting radiation from the sample back to the spectrometer. This process is called remote spectroscopy. This is a reagentless process and relies on the ability to obtain high quality spectra through fibre optic probe.

1.6 Biosensors:

Enormous research and development activities are progressing in the area of fibre optic biosensors (FOBS). FOBS can be divided into two, sensors based on a biocatalyzed reaction and those based on a selective binding reaction[9].

For biocatalytic biosensors, an isolated enzyme is immobilized within the sensing region of an optical fibre. The selective biocatalytic reaction is catalyzed as the

analyte approaches the immobilized enzyme and a product of this reaction is monitored through fibre optic probe. FOBSs have been developed for the detection of ammonia, carbon dioxide, oxygen, hydrogen peroxide etc.

Research and development activities on FOBSs based on selective binding proteins are also employed on a large scale. Binding reactions between antibodies and antigens, lectins and carbohydrates, membrane receptors and their substrates have been used as chemical recognition components for sensors. Evanescent waves are also used for these types of sensors by replacing cladding and covalently attaching the antibody to the exposed fibre core. Evanescent field excites the labelled molecules within the evanescent zone surrounding the exposed core. If the antibody is labelled, a large fluorescence signal is recorded in the absence of antigen. Binding of the antigen to the antibody either quenches or enhances the measured fluorescence intensity.

1.7 Distributed Optical Fibre Sensors (DOFS):

Distributed optical fibre sensing is a technique, which utilises the very special properties of the optical fibre to make simultaneous measurement of both the spatial and temporal behaviour of a measurand field.[4] This technique provides a new level of understanding, especially in the case of large structures and leads to a finer monitoring of the behaviour of the measurand. Using this DOFS, we can measure spatial distribution with a resolution of 0.1-1 m over a distance of 100 m and to an accuracy of 1 %.[4] With the aid of these sensors, it becomes possible to determine the value of a desired measurand continuously as a function of position, along the length of a suitably configured fibre having arbitrary large spatial resolution. The temporal variation is determined simultaneously from the time dependence of the signal. Thus this technique offers many attractive possibilities for industrial and research applications.

It is very important and necessary to get accurate information of the spatial/temporal behaviour of strain and temperature from the point of view of both safety monitoring and of improved understanding of the behaviour under anomalous conditions in dams, bridges, multi-storied buildings, air crafts, space crafts, boilers, chemical pressure vessels, electrical generators etc. The flexibility of fibre makes it relatively easy to install over the chosen measurement path and thus allows retrospective fitting unlike other sensor systems.

A detailed description and the variety of methods involved in the development of DOFSs can be found elsewhere.[4]

1.8 Conclusion:

Details regarding a number of fibre optic sensors developed by intensity modulation, phase modulation, polarisation modulation are available in the literature. The intensity modulated sensors are found to be very easy to design and develop even though they do not have very high sensitivity. The succeeding chapters of my thesis deal with the design and development of some fibre optic sensors based on intensity modulation.

Chapter 2

EVANESCENT WAVE FIBRE OPTIC SENSORS: THEORY

Abstract

This chapter gives a theoretical picturization of the evanescent field at the core-cladding interface of dielectric waveguides and deals with the theoretical modelling of evanescent wave based fibre optic sensors. We also discuss some crucial parameters which are very much essential in the design of a variety of intensity modulated evanescent wave fibre optic sensors.

2.1 Introduction:

The exponentially decaying evanescent fields in the lower index region of a waveguide have been offering high potential in the design and fabrication of a variety of sensors. We can find extensive research and development activities in the literature which exploits the evanescent waves in both cylindrical and planar waveguides.[5,21-24,28,31-37] As indicated in the previous chapter, this technique offers a lot of advantages. This chapter gives a brief note on the theoretical understanding of the evanescent waves both in planar and cylindrical waveguide structures. It also provides the design aspects of optical fibre based evanescent wave absorption sensors, which form the basis of our investigations. In the literature we can find different designs of these fibre sensors for the enhancement of sensitivity as well as the dynamic range of measurands. B D Gupta et al in their paper discuss the effect of launching condition and geometry of the sensing region on the sensitivity of fibre optic evanescent wave absorption sensors.[25] Another design for the evanescent wave absorption sensors is based on U-shaped fibre sensor probes.[38,39] Nidhi Nath and Sneh Anand in their recent work on evanescent fibre optic fluorosensor have theoretically analysed signal acquisition from straight fibre and tapered fibre.[40] A fibre optic sensor probe consisting of a uniform core sandwiched between two linear tapered region forms another category.[41]

2.2 Evanescent waves in planar wave guide structure:

The mechanism by which the rays are confined within a waveguide is by total internal reflection and in order to visualise this phenomena closely at the guide cladding interface, it becomes necessary to approach electromagnetic wave theory model at the interface.[42] The simplest way to understand the concept of optical propagation through the waveguide is by considering the case of planar waveguide structure.

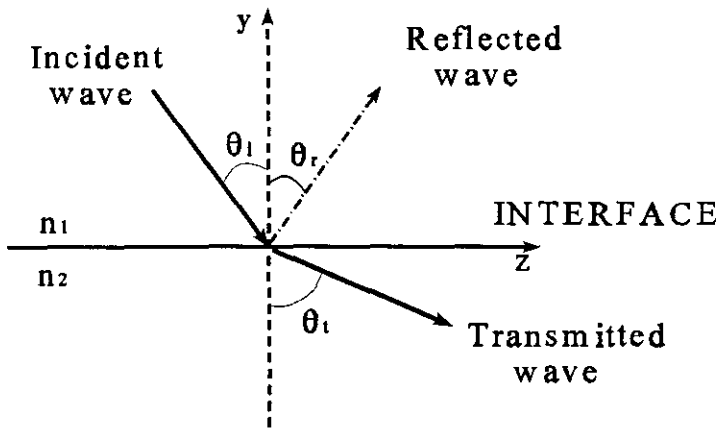


Figure 2.1 Light ray incident on the boundary between two dielectric media with refractive indices n_1 and n_2. Where $n_1 > n_2$ and θ_i ,θ_r , θ_t are angles of incidence , reflection and transmission respectively.

When an electromagnetic wave is incident on the boundary between two dielectric media whose refractive indices are n_1 and n_2, then in general, a portion of that wave is reflected and reminder transmitted.

$$\Delta^2\mathbf{E}+n^2k_0^2\mathbf{E}=0 \qquad (1)$$

represents the wave equation which is incident from the higher index (n_1) region to the lower index (n_2) region. The wave is incident on the interface at an angle θ_i to the normal and the reflected and transmitted waves are at angles θ_r and θ_t respectively. These angles are related by the equations

$\theta_i = \theta_r$

$$\frac{\mathrm{Sin}\theta_i}{\mathrm{Sin}\theta_t} = \frac{n_2}{n_1} \qquad (2)$$

Across the boundary Maxwell's equation require that both the tangential components of **E** and **H** and the normal components of **D** and **B** are continuous.

$$\mathbf{n} \times (\mathbf{E}_2 - \mathbf{E}_1) = 0$$

$$\mathbf{n} \times (\mathbf{H}_2 - \mathbf{H}_1) = 0$$

$$\mathbf{n} \cdot (\mathbf{D}_2 - \mathbf{D}_1) = 0$$

$$\mathbf{n} \cdot (\mathbf{B}_2 - \mathbf{B}_1) = 0 \qquad (2)$$

Solving the wave equation with suitable approximations, we will get Fresnel's equations and these equations deal with the magnitudes of the transmitted and reflected electric fields relative to the incident field.[43]

$$\frac{E_r^{\perp}}{E_i^{\perp}} = \frac{n_1 \cos\theta_i - n_2 \cos\theta_t}{n_1 \cos\theta_i + n_2 \cos\theta_t}$$

$$\frac{E_r^{II}}{E_i^{II}} = \frac{n_1 \cos\theta_t - n_2 \cos\theta_i}{n_1 \cos\theta_t + n_2 \cos\theta_i}$$

$$\frac{E_t^{II}}{E_i^{\perp}} = \frac{2n_1 \cos\theta_i}{n_1 \cos\theta_i + n_2 \cos\theta_t}$$

and

$$\frac{E_t^{II}}{E_i^{II}} = \frac{2n_1 \cos\theta_i}{n_1 \cos\theta_t + n_2 \cos\theta_i} \qquad (4)$$

where E^{II} and $E^{\perp}$ represent electric field vectors parallel and perpendicular to the plane of incidence.

In the situation of total internal reflections, ie, when $\theta_i > \theta_c$ where $\theta_c = \sin^{-1}\frac{n_2}{n_1}$, there will not be a transmitted wave in the second medium. Although all the energy in the beam is reflected when $\theta_i > \theta_c$, there is still a disturbance in the second medium, whose electric field amplitude decays exponentially with distance away from the boundary.

We can derive an expression for this decay by considering the phase factor P of the transmitted wave. P at a point '**r**' may be written as

$$P = \exp i (\omega t - \mathbf{k}_t \cdot \mathbf{r}) \quad (5)$$

where, k_t is the wave vector associated with the transmitted wave.

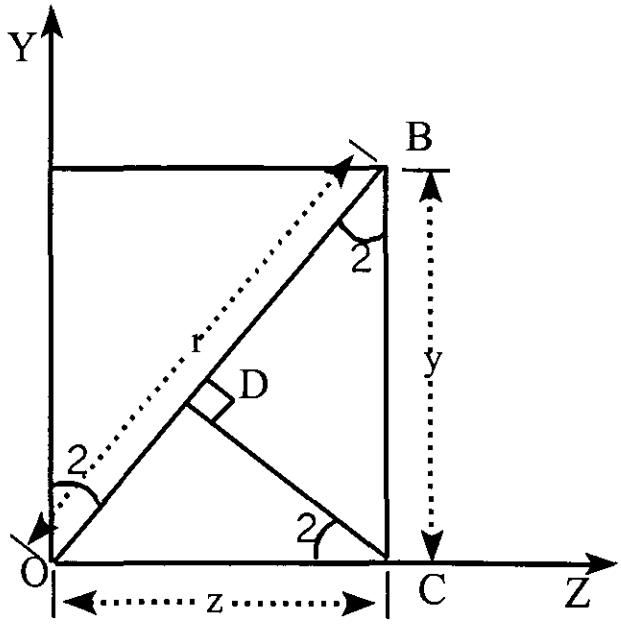


Figure 2.2 Illustration of the relationship between the rectangular coordinates y and z and the distance r measured from the origin O.
$r = z \sin\theta + y \cos\theta$

From figure 2.2, r may be written as, $r = z \sin\theta_t + y \cos\theta_t$

Substituting this in equation 5, we get

$$P = \exp i [\omega t - k_t (z \sin\theta_t + y \cos\theta_t)]$$

$$= \exp i [\omega t - \frac{2\pi n_2}{\lambda_0} (z \sin\theta_t + y \cos\theta_t)] \quad (6)$$

where λ_0 is the wavelength of radiation in vacuum.

We have $\cos\theta_t = (1 - \sin^2\theta_t)^{1/2}$

From equation 2

$$\sin^2\theta_t = \frac{n_1^2}{n_2^2}\sin^2\theta_i$$

$$\therefore \cos\theta_t = [1 - (\frac{n_1}{n_2})^2 \sin^2\theta_i]^{1/2}$$

when $\theta_i > \theta_c$, $\sin\theta_i > \frac{n_2}{n_1}$ and $\cos\theta_t$ then becomes wholly imaginary.

Then $\cos\theta_t = \pm i\, B$ (7)

where $B = [(\frac{n_1}{n_2})^2 \sin^2\theta_i - 1]^{1/2}$ (8)

Substituting in equation 6 for $\sin\theta_t$ and $\cos\theta_t$.

$$P = \exp i\left[\omega t - \frac{2\pi n_2}{\lambda_0}\left(z\frac{n_1}{n_2}\sin\theta_i + (\pm iB)y\right)\right]$$

$$= \exp\left(\pm B\frac{2\pi n_2}{\lambda_0}y\right)\exp i\left(\omega t - \frac{2\pi n_1 \sin\theta i}{\lambda_0}z\right) \quad (9)$$

Thus, in the y direction the wave either grows or decays exponentially with distance. The former situation is obviously a non-physical solution and we must choose $\cos\theta_t = -iB$. The decay with distance in the second medium is given by the factor F(y)

where $F(y) = \exp\left(-\frac{2\pi n_2}{\lambda_0}By\right)$

$$= \exp\left\{-\frac{2\pi n_2}{\lambda_0}\left[\left(\frac{n_1}{n_2}\right)^2 \sin^2\theta_i - 1\right]^{1/2} y\right\} \quad (10)$$

Usually F(y) decays rapidly with y. However, when θ_i is very close to θ_c, then

$[(\frac{n_2}{n_1})^2 \sin^2\theta_i - 1]^{1/2}$ will be close to zero and the disturbance may extend an appreciable distance into the second medium. This part of the wave in the second medium is the evanescent wave.

2.3 Evanescent waves in cylindrical waveguide structure:

Consider the electromagnetic waves propagating along a cylindrical fibre as shown in figure 2.3

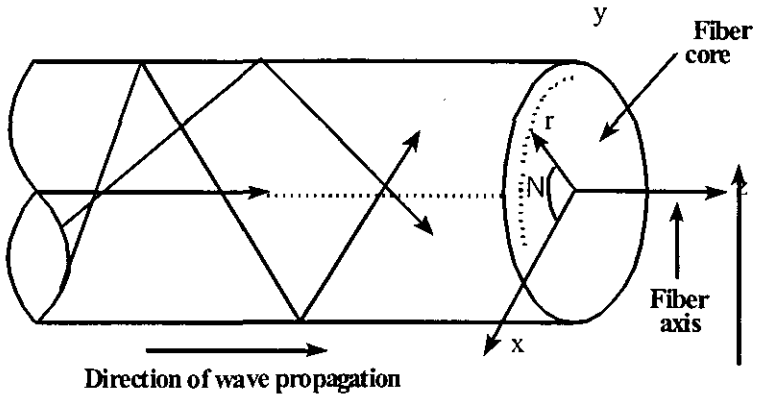


Figure 2.3 Cylindrical coordinate system used for analysing wave propagation in an optical fibre

The wave equation in cylindrical co-ordinate system is given by.[44,45]

$$\frac{\partial^2 E_z}{\partial r^2}+\frac{1}{r}\frac{\partial E_z}{\partial r}+\frac{1}{r^2}\frac{\partial^2 E_z}{\partial \phi^2}+q^2 E_z=0 \qquad (11)$$

and $$\frac{\partial^2 H_z}{\partial r^2}+\frac{1}{r}\frac{\partial H_z}{\partial r}+\frac{1}{r^2}\frac{\partial^2 H_z}{\partial \phi^2}+q^2 H_z=0 \qquad (12)$$

These two equations contain either E_z or H_z. This implies that the longitudinal components of E and H are uncoupled and can be chosen arbitrarily provided that they satisfy equations 1 and 2. Mode solutions can be obtained in which either E_z or $H_z = 0$. When $E_z = 0$ modes are called transverse electric or TE modes and when $H_z = 0$, transverse magnetic or TM modes result. Hybrid modes exist if both E_z and H_z are non zeros. They are designated as HE or EH modes. We can solve the above two equations by variable seperable method. The solution of the equation is of the form

$$E_z = A\, F_1(r)\, F_2(\phi)\, F_3(z)\, F_4(t) \qquad (13)$$

where time and z – dependant factors are given by $F_3(z)F_4(t) = e^{j(\omega t - \beta z)}$

Because of the circular symmetry of the waveguide, each field component must not change when the co-ordinate ϕ is incresed by 2π. Thus we assume $F_2(\phi) = e^{jv\phi}$, where the constant 'v' can be positive or negative. Substituting these in wave equation for E_z we will get

$$\frac{\partial^2 F_1}{\partial r^2} + \frac{1}{r}\frac{\partial F_1}{\partial r} + \left(q^2 - \frac{\nu^2}{r^2}\right)F_1 = 0 \qquad (14)$$

This is a differential equation for Bessel function. An exactly identical equation can be derived for H_z as well. Equation 14 is solved for the regions inside the core and outside the core. For the inside region the solutions for the guided modes must remain finite as r $\rightarrow$ 0, whereas in outside, the solutions must decay to zero as r $\rightarrow \infty$. Thus for r < a, the solutions are Bessel functions of first kind of order v.

$$E_z(r < a) = AJ_\nu(ur)e^{jv\phi}e^{j(\omega t - \beta z)} \qquad (15)$$

$$H_z(r < a) = BJ_\nu(ur)e^{jv\phi}e^{j(\omega t - \beta z)} \qquad (16)$$

where $u^2 = k_1^2 - \beta^2$, $k_1 = 2\pi n_1/\lambda$ and A and B are arbitrary constants.

Outside the core, the solutions are given by modified Bessel functions of the second kind, $K_v(wr)$, where $w^2 = \beta^2 - k_2^2$ and $k_2 = 2\pi n_2/\lambda$.. The expression for E_z and H_z outside the core are given by

$$E_z(r > a) = CK_\nu(wr)e^{jv\phi}e^{j(\omega t - \beta z)} \qquad (17)$$

$$H_z(r > a) = DK_\nu(wr)e^{jv\phi}e^{j(\omega t - \beta z)} \qquad (18)$$

where C and D are arbitrary constants.

From the definition of modified Bessel function, it is seen that $K_v(wr) \rightarrow e^{-wr}$ as wr $\rightarrow \infty$. The modified Bessel function decays exponentially with respect to r. Hence $K_v(wr)$ must go to zero as r$\rightarrow \infty$.

The field distribution in the core and cladding regions have the same form and the electric field pattern corresponds to a non-uniform wave travelling in the z-direction.

Moreover, specifically, it is a standing-wave pattern in the fibre core and a decaying or evanescent wave in the cladding region as illustrated in figure 2.4.[42]

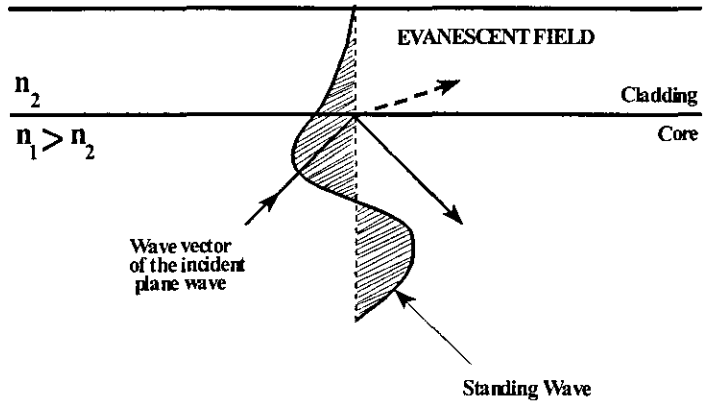


Figure 2.4 Illustration of standing wave pattern and exponentially decaying evanescent wave

2.4 Fibre optic evanescent wave absorption sensors:

Exponentially decaying evanescent fields were utilised for developing different types of intensity modulated fibre optic sensors. This includes optical fibre based refractometers to measure refractive indices to a high degree of accuracy.[31,46] Variation in the refractive index of the uncladded region of the cylindrical waveguides were used for making different sensors to detect or measure different physical or chemical variables. Lisa et al developed evanescent wave immunosensor. Here, the toxin from clostridium botulinum and pseudexin has been detected using the above principle.[47] Another type of evanescent wave fibre sensor was based on excitation and detection of fluorescence using evanescent waves.[29] However, most commonly used fibre optic evanescent wave sensors are based on evanescent wave absorption phenomena.[5,21-23, 25,27,28,38,39,48]

Evanescent waves in the cladding region were exploited for developing evanescent wave absorption sensors. This is achieved by removing a certain region of

the cladding of the fibre and allowing interaction with the external medium. Evanescent field absorption occurs when the medium, which forms the cladding of the waveguide absorbs the light at the wavelength being transmitted through the fibre. Compared to other sensing methods these evanescent wave fibre optic sensors have a lot of advantages, which have motivated different groups to work in this field. In evanescent wave fibre optic sensors, the interrogating light remains guided in the sensor and no coupling optics are required at the sensing region. Also, these sensors offer the possibility to achieve a considerable miniaturisation. The technique provides enhanced sensitivity over conventional bulk optics attenuated total internal reflection (ATR) crystals.[29] Also, in bulk optics method, it is often difficult to perform accurate absorption measurements on highly absorbing or scattering media. But fibre optic evanescent wave sensors are suitable for such samples because the effective path length in this case is small. Also, this technique is much less sensitive to scattering. Fibre optic sensors offer high potentiality for remote operation and for on-line measurements of different physical and chemical parameters.

There are two different types of evanescent wave absorption sensors. The first one is direct spectroscopic evanescent wave sensor. In this type, evanescent field at the lower index region can interact directly with the analyte, if the wavelength of guided waves coincides with the absorption band of the measurand. The second type is called reagent mediated evanescent wave sensors. Here, an intermediate reagent, which responds optically to the analyte, may be attached to the waveguide. This type of sensor provides greater sensitivity than direct spectroscopic devices.[29]

Design of evanescent field absorption based sensor devices requires a knowledge about certain parameters. These design parameters play a crucial role in determining the sensitivity, dynamic range etc. of fibre optic sensors. The degree of penetration of evanescent field into the low refractive index medium is very important. This quantity is called penetration depth of the evanescent field, d_p. This is defined as the perpendicular distance from the core-cladding interface at which the electric field

amplitude has become 1/e of its value at the waveguide interface. If E_0 represents the electric field amplitude at the interface, after a distance d_p it falls to

$$E = E_0 \exp\left(-zd_p\right)$$

The magnitude of the penetration depth is

$$d_p = \frac{\lambda}{2\pi n_1\left[\sin^2\theta - \left(n_2/n_1\right)^2\right]^{1/2}}$$

λ is the wavelength, θ is the angle of incidence to the normal at the interface, n_1 and n_2 are the refractive indices of denser and rarer media respectively.[49]

Another critical parameter, which has a prominent role in the design is the evanescent power that resides in the cladding. This power fraction of the total guided power is also very important both in fibre refractometers and in evanescent field absorption sensors. This quantity is given by[23]

$$r = \frac{P_{clad}}{P_{total}}$$

This fraction is determined by the fibre V-parameter. The fibre V parameter is given by

$$V = \frac{2\pi\rho}{\lambda} NA$$

where ρ is the fibre core radius and NA is the numerical aperture = $\left(n_1^2 - n_2^2\right)^{1/2}$ and λ is the propagation wavelength.

Analysing the evanescent power for different fibres we can see that substantial values of 'r' can be achieved for single mode fibres. But for fibres with high V-parameter, the average fractional power in the cladding is very low. The value of 'r' is maximum for modes close to cut-off and for higher order modes.

Even though single mode fibres have higher evanescent wave power fraction and higher sensitivity, multimode fibres can also be used for developing evanescent wave sensors as multimode fibres have greater power throughput and easiness in handling.[29]

For weakly guiding ($n_1 \cong n_2$) multimode fibres, the average value of 'r' is[23]

$$r = \frac{4\sqrt{2}}{3V}$$

Since the amount of absorption depends both on the amplitude of evanescent field in the sample medium and the number of reflections within the sensing region, the amplitude of evanescent field increases dramatically for incident angles approaching waveguide – sample critical angle. The number of reflections is inversely proportional to the waveguide thickness. Removal of cladding results in V-number mismatch between the cladded portion and the sensing portion of the fibre.[40] V-number, which determines the mode capacity of the fibre is lower for the cladded region than that for the sensing region. The numerical aperture of the fibre is considerably less than that at the core-sample region. There are different techniques adopted by different groups to enhance the evanescent power. Also, there are strong theoretical models suggested by different groups to tackle this problem and to enhance the transmission of higher order modes through the fibre by launching selected modes in the multimode fibre.[23,25,26]

The power transmitted by an optical fibre where cladding has been locally replaced by an absorbing medium is given by[28]

$$P(z) = P(0)\exp(-\gamma z)$$

P(0) is the power transmitted through the fibre in the absence of an absorbing medium and γ is the evanescent wave absorption coefficient, z is the distance along the uncladed length.

The evanescent wave absorption coefficient γ is related to the bulk absorption coefficient α,

$$\gamma = r\alpha$$

where r is the fraction of the power outside the fibre core when all bound modes are launched in the multimode fibre.

Then output power through the fibre is given by the equation

$$P(z) = P(0)\exp(-r\alpha z)$$

The evanescent wave absorbance is given by $A = \log_{10} \frac{P(0)}{P(z)}$

$$\therefore A = \frac{\gamma L}{2.303} = \frac{r\alpha L}{2.303}$$

where L is the length of the uncladded region of the fibre.

V Ruddy et al suggested a model for the enhancement of transmission of higher order modes through the fibre by launching only selected modes through the fibre. Spatial filtering was used to restrict modes that were having substantial power in the evanescent field in the uncladded region.[23]

Evanescent absorption coefficient is given by

$\gamma = NT$

N is the number of reflections per unit length and T is the Fresnel transmission coefficient at the interface of loss-less core and lossy cladding. The refractive index of lossy cladding is given by $n_2 - ik$. The bulk absorption coefficient of the cladding material is given by

$\alpha = \frac{4\pi k}{\lambda}$, where k is extinction index.

In a weakly guiding fibre ($n_1 \cong n_2$) the relationship between evanescent absorption coefficient γ and bulk absorption coefficient α of the lossy cladding is given by

$$\frac{\gamma}{\alpha} = \frac{1}{V}\left(\frac{\theta_z}{\theta_c^1}\right)^2 \frac{1}{\sqrt{1 - \left(\theta_z / \theta_c^1\right)^2}}$$

V – normalised frequency parameter of the waveguide, θ_z is the angle the ray makes with the core axis, θ_c^1 is the complementary critical angle ($\cos^{-1} n_2/n_1$)

In the case of evanescent field sensors in aqueous solutions, the difference in refractive index between core and cladding at the launch end is very much smaller than

the refarctive index difference at the core-sample region (at the sensing region). In that case the weakly guiding approximation is not valid. In such a condition the value of T can be obtained as

$$T = \frac{\alpha \lambda n_2 \sin\theta_z}{\pi n_1^2 \sin^2\theta_c^1 \sqrt{\cos^2\theta_z - \cos^2\theta_c^1}}$$

and $N = \frac{\tan\theta_z}{2\rho}$, ρ is the fibre core radius

The ratio of evanescent absorption coefficient to bulk absorption coefficient becomes

$$\frac{\gamma}{\alpha} = \frac{\lambda n_2 \cos\theta \cot\theta}{2\pi\rho n_1^2 \cos^2\theta_c \sqrt{\sin^2\theta - \sin^2\theta_c}}$$

where θ is the angle between the ray and the normal to the interface $\theta = \pi/2 - \theta_z$ and θ_c is the critical angle for the two media. $\theta_c = \sin^{-1} n_2/n_1$

We have discussed two different theoretical aspects in the design of evanescent wave fibre optic sensors, viz. uniform core with all bound modes launched and uniform core with only selected modes launched into the fibre. But, we have carried out our investigations based on the former theoretical framework only. The following chapters discuss our experimental studies based on this framework.

2.5 Conclusion:

Theoretical outline for the evanescent waves in planar waveguides and cylindrical waveguides has been given. Some aspects of the theoretical background in the case of fibre optic evanescent wave absorption sensors have also been discussed.

Chapter 3

OPTICAL FIBRE BASED SENSOR TO DETERMINE THE DEPOSITION RATE OF THIN FILMS

Abstract

This chapter illustrates a novel method for the in-situ measurement of deposition rate and thickness of thin films. Evanescent field in the uncladded region of a multimode fibre is exploited for the sensor design. Utility of this sensor is described in the case of pulsed laser deposition of silver thin films obtained by irradiating a Q-switched Nd:YAG laser on a silver target. This chapter explicitly establishes the use of this new approach in the deposition rate measurement as well as for the thickness monitoring of thin films prepared by some of the conventional deposition techniques as well.

3.1 Introduction:

The structure and many other important properties of thin films are dependent on their nucleation and growth processes. These are controlled by a number of parameters such as deposition rate, thickness, velocity, angular distribution, nature of species of the impinging vapour, composition of ambient gas, substrate temperature etc.[50-54] Among these factors, most significant parameters are the deposition rate and thickness of thin films. Also, these factors influence the reproducibility of the properties of thin films and the same can be achieved by precisely controlling or monitoring the above mentioned parameters. Thus, deposition rate measurement and on-line thickness monitoring have become essential elements of thin film preparation. Sensing devices that allow measurements during the deposition process are referred to as either thickness or rate monitors. Monitoring devices have been constructed by different individual investigators to suit their specific purpose and numerous designs have appeared in this regard. Some of the techniques for in-situ deposition rate measurements adopted at present are discussed in this section.

There are numerous techniques such as resistance monitors, capacitance monitors, quartz crystal monitors, ionisation monitors, optical monitors etc. to monitor the deposition rate measurements. Most of these methods are suitable to certain specific thin film deposition techniques or peculiar to certain class of materials. Also, these techniques have several demerits and hence are inadequate in general applications.

3.1.1 Resistance Monitors:

This is a very simple method and here the deposition rate or thickness is measured in terms of resistance variation of thin films. The resistance of thin film can be measured very easily by making the film as one arm of a dc or ac Wheat-stone's bridge. For a given value of the ratio of arms of the bridge, the film resistance is proportional to a variable resistance that can be measured by automatically recording the potential across it. If resistivity ρ of a film material remains constant throughout the deposition, the film thickness d can be continuously monitored as, $d = \frac{\rho l}{Rw}$

where, l, w are length and width of the thin film respectively. R is the resistance of thin film measured.[51]

The disadvantage of this method is that it is only applicable to metallic and low resistivity semiconductor films. Also, since resistivity of semiconductor films is very sensitive to deposition conditions this method is applicable only for comparison of film thickness rather than for absolute measurements. This method is very complex in ultra thin and structurally discontinuous films (<100Å). Moreover, their reliability is also very poor.

3.1.2 Capacitance Monitors:

Capacitance monitors are used to measure the thickness of dielectric thin films by directly monitoring the electrical capacitance of a capacitor configuration, which is placed in the path of vapour stream from the evaporant. The rate of evaporation can also

be measured by monitoring the changes in the capacitance of a parallel plate condenser due to the changes in the dielectric constant resulting from the presence of the vapours from the evaporant.[50] However, this method is not very sensitive and hence requires careful measurements. Also, this method is mainly applicable to the deposition rate measurements of dielectric thin films. Another serious drawback of this monitor is that it may be subject to spurious effects due to strong electrical charges in the vapour and in the vacuum chamber.

3.1.3 Quartz Crystal Monitors:

A quartz crystal monitor (QCM) can be generally used for monitoring the deposition rate of metals, non-metals, multicomponent thin films etc. This relies on the resonant frequency change of the quartz crystal oscillator due to mass loading. Mass added on the crystal shifts the oscillating frequency irrespective of the density, elastic constants or stiffness of the adsorbed material.[50]

But there are limitations to this technique also. The maximum sensitivity of a quartz crystal monitor is limited by variations in the crystal frequency due to temperature, oscillator drive level and changes in the oscillator circuit. Besides these drawbacks, it is necessary to use suitable radiation shields so that only active area of QCM is exposed to the source. Otherwise, the temperature will rise because of the heat of condensation liberated during the deposition of the vapour. Also, water cooling of the crystal holder is essential to avoid the excessive heating due to lengthy duration of deposition from extended sources.

3.1.4 Ionization Monitors:

Evaporation rate can be monitored by ionizing the vapour from the evaporant and measuring the resultant ion current.[50] The ion current is proportional to the total number of vapour atoms and their ionization probability. An ionization monitor consists of a triode type ionization gauge. The description of a typical ionization monitor is as

follows. It consists of a thermal source or a filament for producing electrons, a spiral wire grid (anode) at a positive potential for acceleration of electrons which also ionize the vapour in the region between anode and a negatively biased collector wire. This collector wire collects the ions formed and hence cause the ion current.

There are a number of disadvantages for this monitor. It is necessary to heat the anode and the collector to prevent deposition of the vapours on them; or else they have to be cleaned periodically. Another drawback is that the vapour may carry negative charges which won't come into consideration, as the collector is at a negative potential. Moreover, residual gas atoms present in the chamber may give an appreciable background ion current, which may limit the accuracy of the monitor.

3.1.5 Optical Monitors:

Optical phenomena such as light absorption, transmittance, reflectance, interference etc. can be utilised to monitor the growth of films during vacuum deposition. The necessary equipment is relatively simple and consists of a light source and a detector. Both of them are located outside the vacuum chamber, which is provided with suitable windows. Metal films may be observed by transmittance measurements when they are deposited onto a transparent substrate. Reflectance measurements can also be carried out on metal films. The monitoring of transparent films exploits the periodic fluctuation in light intensity which arise from multiple reflections within the film and subsequent interference. The conditions for constructive and destructive interference may depend on the refractive indices of film and substrate materials. This method is mainly used for monitoring and controlling the deposition rate of multilayer dielectric films. Transmittance and reflectance monitoring techniques are most often employed when thin films are deposited for optical purposes such as beam splitters, mirrors, antireflection coatings and interference filters.[51] Optical methods have the advantage that they are generally non-contact in nature and hence in-situ measurement can be performed conveniently without breaking vacuum.

Intensive search for a suitable general method which avoids most of the demerits mentioned earlier for both the deposition rate monitoring and in-situ thickness measurement is in progress. Here, in the subsequent sections, we present a novel approach in this direction.

3.2 Fibre optic sensor:

Exponentially decaying evanescent fields in the uncladded region of a multimode fibre is exploited for the sensor design. The fibre optic sensor head is kept close and parallel to the substrate on which the thin film is to be prepared. This simple design for the in-situ measurement of deposition rate and thickness monitoring overcomes most of the demerits of the existing deposition monitoring devices. This approach can be employed for the measurement of metallic, nonmetallic and multicomponent thin films. It is safe from spurious effects due to strong electrical charges in the vapour. Neither radiation shield nor water cooling arrangement are required for this optical fibre based sensor device. This simple and reliable method enables us to achieve remote measurements without breaking vacuum in the deposition chamber. The evanescent wave fibre optic sensor (EWFOS) enables one to optimise the deposition conditions to get the required thin film configuration.

In this chapter we discuss the applicability of this fibre optic sensor system for the deposition rate measurement of silver thin films obtained by laser ablation and also for the deposition rate measurement of aluminium thin films, produced by thermal evaporation method. This new tool has already been successfully employed for deposition rate measurement in the case of polypyrrole thin films produced by AC plasma polymerisation method.[6] In this investigation an output power variation of 1μW has been reported corresponding to 0.1 nm deposition.

3.3 Pulsed Laser Deposition:

Pulsed Laser Deposition (PLD) has been established as a technique for the preparation of thin films of various substances ranging from pure elements to multicomponent materials.[54,55] PLD is a very convenient technique for thin film preparation and it offers superior film qualities compared to films deposited by other methods. It involves a simple configuration and the schematic representation of the PLD along with the FOS system incorporated into it is as shown in figure 3.1.

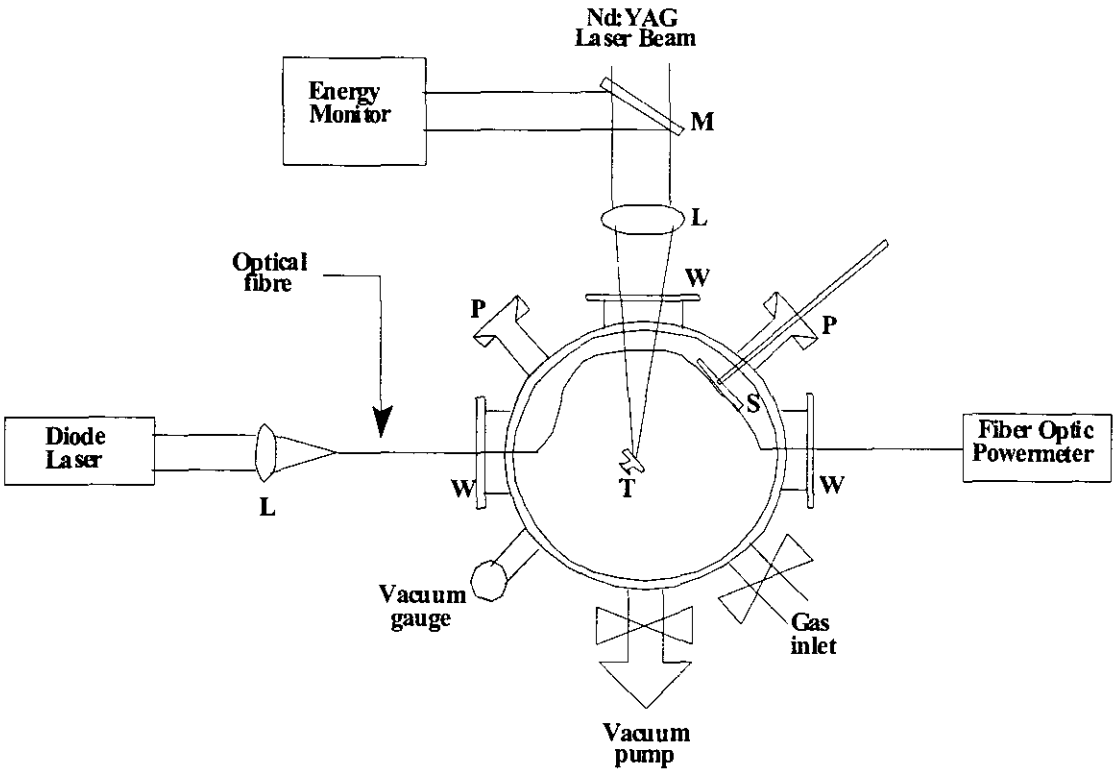


Figure 3.1 Schematic of the Pulsed Laser Deposition (PLD) set-up along with the fibre optic sensor system. M - 10% reflector, L – lens, W – glass window, P – Substrate insertion port, T – rotating target holder, S – glass substrate

Even though the laser-target interaction is a very complex process in terms of theoretical understanding, the interest in PLD is growing fast due to the numerous advantages offered by this method. One of the key features of PLD is its ability to

reproduce the target composition relatively easily under appropriate conditions. PLD offers high flexibility in laboratory scale applications and this can be done in conjunction with other processes like conventional thermal evaporation or glow discharge plasmas. Unlike other deposition methods, PLD involves a number of controlling parameters like laser fluence, repetition rate of laser, laser wavelength etc. for the material deposition.[56-59] Smoother films with correct stochiometry are usually obtained with PLD due to the congruent evaporation. On-line measurement of the deposition rate of the ablated material is essential to establish the optimal film growth as well as for the continuous monitoring of the deposition process.

3.4 FOS to monitor the rate of pulsed laser deposition:

The schematic of the fibre optic sensor (FOS) system along with the pulsed laser deposition (PLD) set-up is as shown in figure 3.1. The pulsed laser deposition (PLD) was achieved by focusing a Q-switched Nd: YAG laser (Quanta Ray DCR-11) with a convex lens of focal length 0.5 m onto a polished silver target (spot radius = 50 μm) at an angle of 45^0 with respect to the target normal. The spot radius was kept the same throughout the course of the investigation. The target was a silver disc having diameter 0.015 m and thickness 0.001 m fixed to a target holder. The target was rotated using a DC motor in order to avoid multiple hits at the same location as well as to avoid splashing. Also, the laser was focussed to a larger radial distance from the target centre in order to remove the heavy mass particulates and to obtain congruent evaporation.[54] A cleaned glass substrate was kept in parallel with the target surface (perpendicular to the plasma plume) at a particular distance from it. Target and substrate holders were kept inside a plasma chamber that can be evacuated to a pressure in the range of 10^{-3} mbar.

A multimode optical fibre (200/380 μm) with polished end faces having an uncladded sensing region of length 0.01 m was placed close and parallel with the glass substrate so as to receive the ablated material from the target. The two end faces of the fibre were taken through two sealed ports in the plasma chamber walls without breaking the vacuum. The beam from a diode laser (4.25 mW, 670 nm) was focused onto one end

of the fibre and the other end was attached to a commercial fibre optic powermeter (Meggar OTP 50).

Ablation of the target material and subsequent deposition were achieved for two laser fluences and at two different wavelengths viz. 1064 nm and 532 nm (second harmonic of the Nd: YAG laser). The repetition rate of the laser beam was 10 Hz and the vacuum in the chamber was kept the same throughout the course of the investigation. The experiment was also performed for two target-substrate distances.

3.4.1 Results and discussion:

The laser-target interaction produces ablation and the ejected material form a plasma plume, which on condensation causes deposition of thin films of the material of the target on the substrate as well as on the sensor element. As the deposition proceeds, silver was continually deposited on the substrate as well as on the uncladded portion of the fibre. In a typical case the thickness formed, after irradiating 1800 pulses of fundamental wavelength of Nd:YAG laser (1064 nm) having 100 mJ energy, was found to be 650 Å. Thickness of the film formed on the substrate as well as on the uncladded portion of the fibre was more or less the same, since target-substrate distance (0.02 m) closely matches the extent of the plume from the target. The laser beam guided through this fibre encounters evanescent wave absorption in this region of the fibre and the output power decreases, which subsequently shows a saturation behaviour[6]. Here, the theory of light propagation in a conducting isotropic medium is applicable and absorption occurs due to the evanescent wave penetration into the stratified silver. In metals the refractive index is a complex quantity and the imaginary part is preponderant[60] resulting in substantial reduction in output power.

Investigations were carried out at two different wavelengths of the laser viz. 1064 nm and 532 nm. For each of these wavelengths, studies were carried out with different energy densities of the laser beam. Figure 3.2 shows the variation of the fibre output with time for a substrate to target distance of 0.02 m corresponding to laser

wavelengths 1064 nm and 532 nm and at two energy densities. The estimated error in output power was found to be less than 5% for these measurements. Comparison of the slopes of the plots at different energies clearly reveals that there is an increase in the deposition rate with an increase in energy density. The plots also reveal that the time interval within which saturation sets in is lowered as the energy fluence is increased. This observation confirms the fact that the deposition rate increases with increase in energy density of the laser beam.[61] T Venkatesan et al measured the angular distribution of the composition and thickness of a high *Tc* superconducting thin films deposited by pulsed laser deposition (PLD) technique.[56] They observed that angular distribution consisted of two distinct components; a cosθ component and a highly forward-directed component.

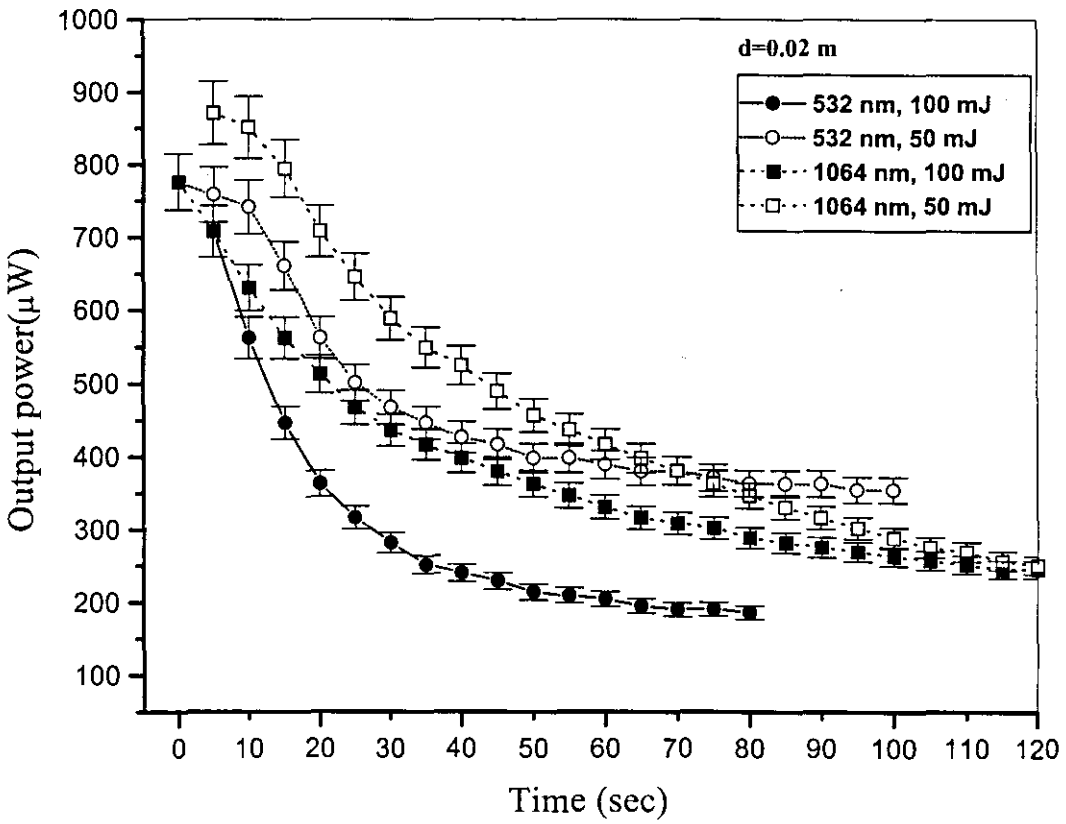


Figure 3.2 Variation of the fibre output with time, d – is the substrate to target distance

The former component results from evaporation and the latter is attributed to secondary ejection process. The evaporated component is nonstoichiometric whereas the forward-directed component has a composition close to that of the target. Only the forward-directed stiochiometric component is found to increase with the laser energy density. The PLD process is mainly a forward-directed process in the sense that the ejected material has a narrow angular distribution.[57] The uncladded sensing region (length 0.01 m) of the fibre essentially receives the forward directed component rather than the evaporated component. The forward directed component has been shown to increase with the laser energy density and deviation from this behaviour occurs mainly at large angles with respect to the target normal.[56] Our results also confirm these observations as we have selected a small exposed length of 0.01 m of the fibre.

The growth rate of Se films has been shown to increase with laser power and decrease with irradiation wavelength.[58] Radiation of wavelength 1064nm penetrates deeply into the target while 532nm light is almost completely absorbed within the first 100 Å. This is also supported by the work of Kautek et al who described an increase in absorbance of deposited superconducting films with decreasing wavelength.[59] Our plots also show that the deposition rate increases at lower wavelengths.

Investigations were also carried out for two different target-substrate distances with 1064nm laser wavelength and the results are given in figure 3.3. A significant decrease in deposition rate with increased distance was observed.

Thus, we have developed a simple and highly sensitive FOS to monitor the rate of pulsed laser deposition of metal thin films. This sensor was also employed to establish the dependence of the deposition rate on some of the control parameters of the irradiating laser beam. However, there is a limitation on the maximum thickness that can be measured with this set-up.

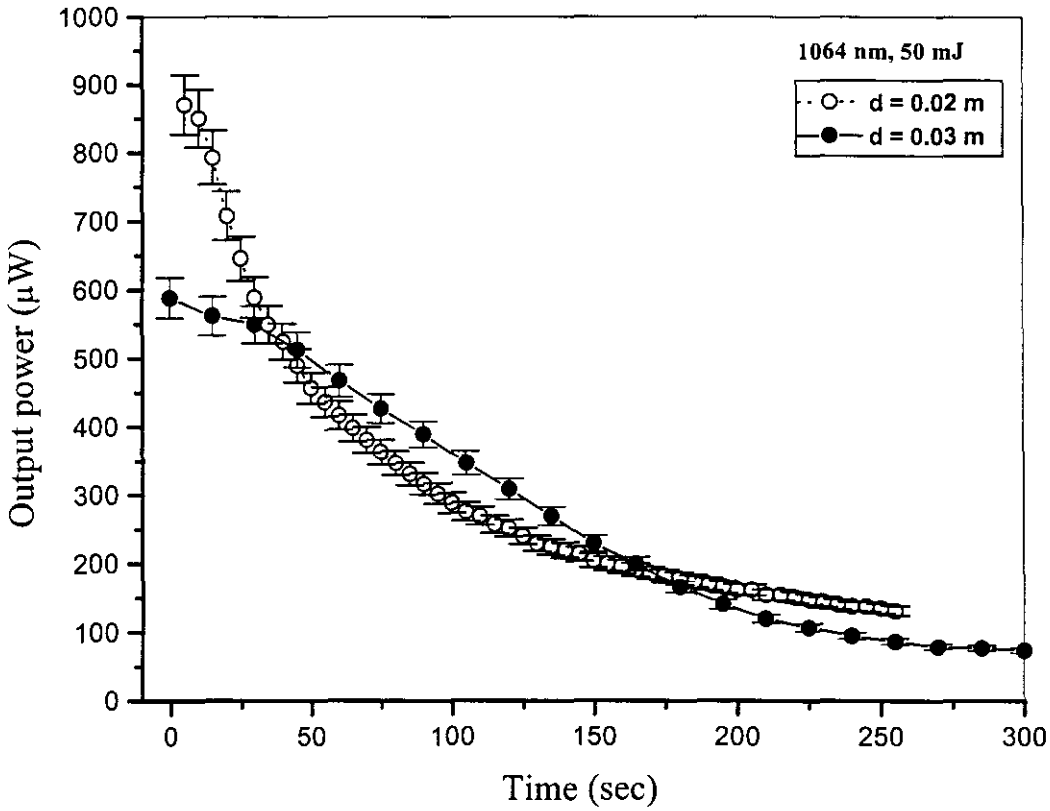


Figure 3.3 Variation of the fibre output with time for different substrate to target distance d.

3.5 Deposition rate monitoring of thermally evaporated aluminium thin films:

The applicability of the newly designed evanescent wave fibre optic monitor for the deposition rate measurement as well as for the in-situ thickness monitoring was verified in the case of thermal evaporation technique as well. This fibre optic monitoring system has the added advantage of remote detection capability. In this section we describe a sensor for deposition rate measurement of aluminium thin films produced by thermal evaporation method.

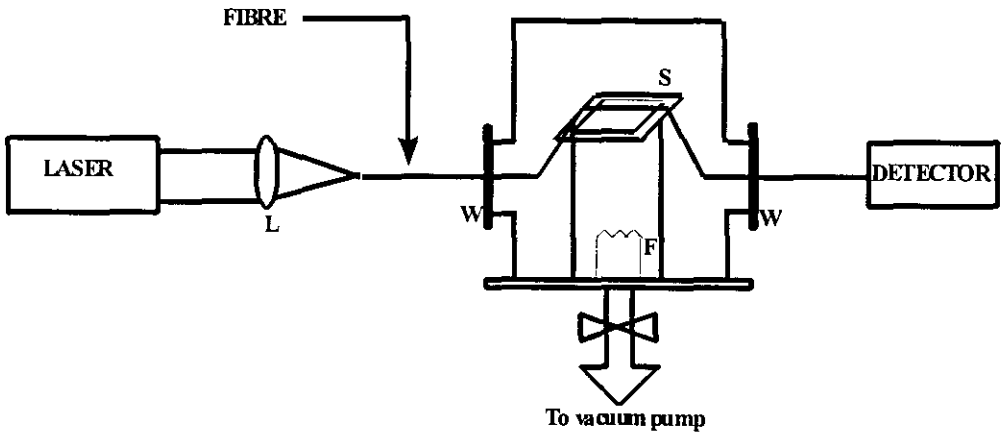


Figure 3.4 Schematic of the experimental set-up. W – window, L – lens, F – Tungsten filament, S – substrate

The schematic of the experimental set-up is shown in figure 3.4. The glass plate on which the film has to be coated was kept at a fixed distance from the tungsten filament. The deposition was carried out at a reduced pressure of 10^{-5} torr. A multimode optical fibre of core diameter 200 μm with cladding removed from a certain length was kept along with the glass substrate where the deposition has to take place. This uncladded portion acts as the sensing element. The fibre ends were taken out through the holes provided in the vacuum chamber without breaking the vacuum. A diode laser emitting at 670 nm and having a power output of 4.25 mW was focussed onto one end of the fibre and the output light from the other end of the fibre was detected using a photodiode detector. The detector consisted of a PIN photodiode (Motorola MFOD 71) followed by an amplifier (TL072).

As high current is allowed to pass through the electrodes, the tungsten filament gets ignited and the aluminium starts to evaporate. As the evaporation proceeds aluminium gets deposited on the glass plate as well as on the uncladded portion of the optical fibre. Laser beam guided through the fibre encounters evanescent wave absorption and the output gets diminished. Here also, the reason for the decrease in output intensity is due to attenuated total internal reflection at the interface between dielectric and metallic media. The output intensity from the optical fibre is measured at

regular intervals of time during the deposition of thin film on the uncladded region of the fibre. Figure 3.5 gives a typical plot for the output voltage variation with time.

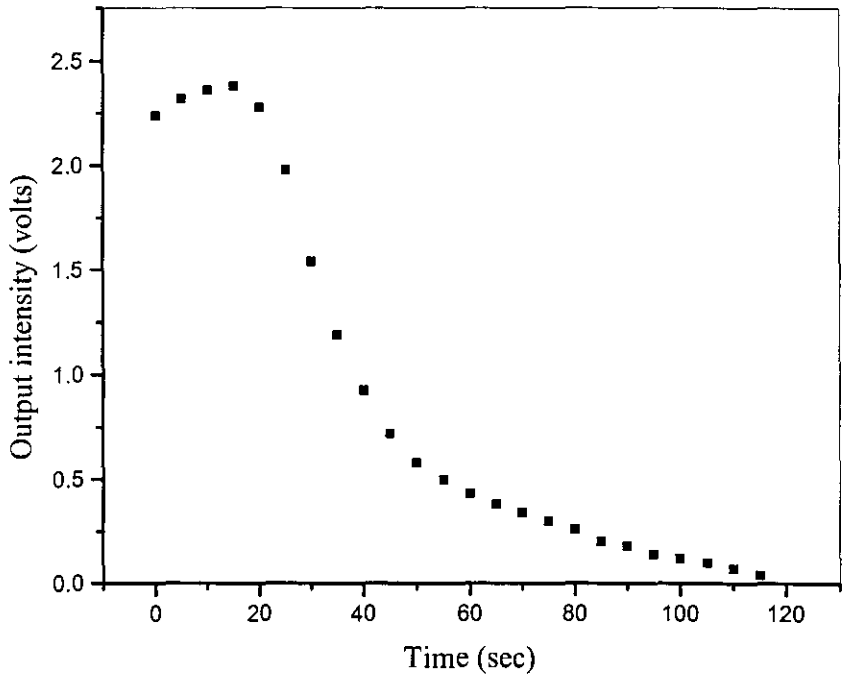


Figure 3.5 Variation of the output voltage with time

Here also, the deposition rate depends on a number of parameters like inter electrode voltage, the current through the tungsten filament, the time duration for which the voltage is applied between the electrodes, the distance between the source of evaporation and substrate etc. With proper calibration, within the linear range of the response curve, we can construct a fibre optic sensor for the measurement of thickness of metallic thin films. Even in this method there is a limit to the thickness that can be measured and the device can be reused only after changing the fibre. However, this novel technique eliminates most of the drawbacks offered by the conventional thickness monitors.

3.6 Conclusion:

In this chapter we have described a novel and convenient method for in-situ thickness monitoring of thin films. This is an effective tool in thickness monitoring as well as the deposition rate measurement of a wide variety of materials and is equally applicable to different types of deposition techniques.

Chapter 4

GLUCOSE CONCENTRATION MEASUREMENT USING FIBRE OPTIC SENSOR

Abstract

Design and development of an evanescent wave fibre optic sensor for the determination of glucose concentration is described in this chapter. This simple and inexpensive optical fibre based device has been found to be very sensitive at low glucose concentrations with saturation at about 4 gm/litre. This sensor works in a direct fashion and overcomes most of the complexities of the existing techniques for glucose detection. Fabrication details and performance evaluation of a hand held version of the fibre sensor are also given in this chapter.

4.1 Introduction:

The quantitative estimation of glucose is very much essential in different fields of applications like analysis of blood and urine samples,[62] food analysis,[63,64] industries etc. There are a variety of classified chemical methods for the quantitative determination of glucose in blood and urine samples both in normal and pathological states. We can see the continuous efforts by biochemical workers to evolve methods which are more specific, more rapid and require small amount of sample. The majority of methods for the determination of blood glucose are based on the ability of glucose, in hot alkaline solution, to reduce certain metal ions. The extent of reduction is then estimated by photometric, titrimetric or gasometric methods. Some of the methods are Flin and Wu method, Somogyi-Shaffer-Hartmann method, Nelson-Somogyi method etc.[62] Similarly a variety of chemical methods like Benedict's method, Hankin and Van Slyke method etc.[62] can be seen for the quantitative determination of glucose concentration in urine samples. Apart from the above-mentioned classical chemical methods, we can find a different branch, an instrumental method, which involves enzymatic determination of

glucose. Here, the glucose concentration is determined using an enzyme electrode and this method is completely specific and require only a small amount of sample.[65,66] The working principle of this method is that, in the presence of enzyme, glucose oxidase, an aqueous solution of glucose undergoes oxidation to gluconic acid with the formation of hydrogen peroxide that can be determined by anodic oxidation at a fixed potential.[67]

Here, in this chapter we are describing a new approach, an optical fibre based glucose sensor, which works on the principle of evanescent wave absorption phenomenon. Evanescent wave spectroscopy is one among the challenging techniques for monitoring chemical processes as well as detection of chemical and biological species.[21-24,40,47,68-72] In these types of sensors, the transducing mechanism between a chemical or biological measurand and light intensity can be optical absorption or fluorescence. The intensity of the interrogating light wave coming out of the fibre is directly related to species concentration. By making use of proper calibration, the device can be configured for the detection and measurement of glucose concentration. This simple and inexpensive method has a wide range of applications, where quantitative measurement of glucose concentration is necessary and essential. Apart from the biomedical and chemical applications, this sensor can be used for industrial applications that require on-line monitoring of glucose concentration. Like other optical fibre sensing techniques, this evanescent wave glucose sensor has a lot of merits. This method is very sensitive and the device is immune to electromagnetic interference. Besides these features, it can be used in industries with capability for remote sensing.

4.2 Experimental details:

In order to utilise the evanescent waves in a multimode fibre, a known length (0.09 m) of the cladding portion of a multimode plastic clad silica fibre (200/380 μm) is chemically removed. The procedure adopted for removing the cladding of the fibre is as follows. The plastic sheath of a certain portion of the fibre is removed using a blade and this portion of the fibre is immersed in concentrated hydrofluoric acid for a specific period of time. Then we can easily remove the cladding of the fibre. A sensor cell is

designed for taking the test liquids. The cell consists of a cylindrical glass tube of length 0.11m having a diameter 0.01m and the two sides of the tube are closed using two glass plates. Also, the cell is provided with inlet and outlet provisions. The optical fibre is introduced into the container through the holes provided on the side plates and is permanently fixed such that the uncladded portion of the fibre is straight within the container. This uncladded region acts as the sensing element. Figure 4.1 represents the fibre optic sensor (FOS) arrangement employed in the present investigation.

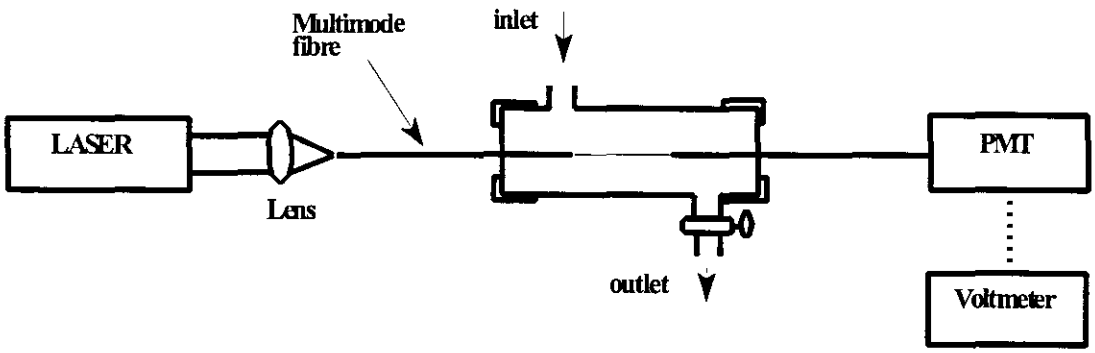


Figure 4.1 Experimental set-up to monitor glucose concentration

A 4.25 mW diode laser (LASERMAX INC.) emitting at 670 nm is launched into one end of the fibre and the light emitting through the farther end is fed into a JETRONICS SO 239 photomultiplier tube (PMT). The ends of the fibre are well polished so as to get optimum coupling. Light from the diode laser is launched into one end of the fibre using a short focal length lens and the transmitted power is detected using the PMT. The glucose solution is prepared in distilled water for various concentrations ranging from 0.001 gm/litre to 10 gm/litre. This glucose solution along with Benedict's reagent (**quantitative reagent**) are mixed in a pre-decided ratio (1:3) and heated on a boiling water bath for five minutes and allowed to cool for some time. This resultant solution acts as the test liquid. When the uncladded region is immersed in the test solution, the evanescent field penetrates into the liquid and interacts with it. As the beam propagates through the fibre it results in the coupling of evanescent wave (EW) to the medium surrounding the core, thereby attenuating the propagating beam.

Usually in fibre optic sensors working on the principle of evanescent wave absorption phenomenon, light of wavelength close to the peak absorption wavelength of the absorbing fluid is launched into the fibre. Then the change in intensity of the transmitted light occuring due to the absorption of the evanescent field penetrating into the medium is measured. The output light is detected using a PMT-voltmeter combination and the change in light intensity is measured in terms of change in voltage. Thus for various glucose concentrations, the output voltages have been measured.

4.3 Results and discussion:

Figure 4.2 shows the variation of the output intensity in terms of change in voltage with glucose concentration. The change in the intensity can be attributed to the evanescent wave (EW) absorption taking place at the operating wavelength (λ = 670 nm) in the sensing region.

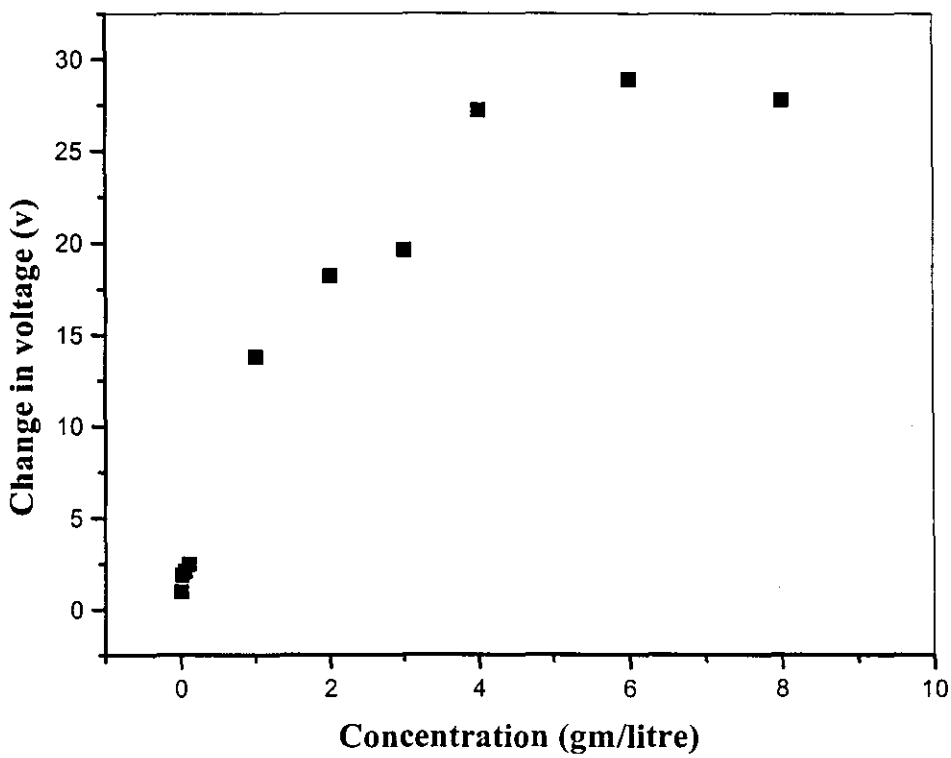


Figure 4.2 Variation of output light intensity with glucose concentration.

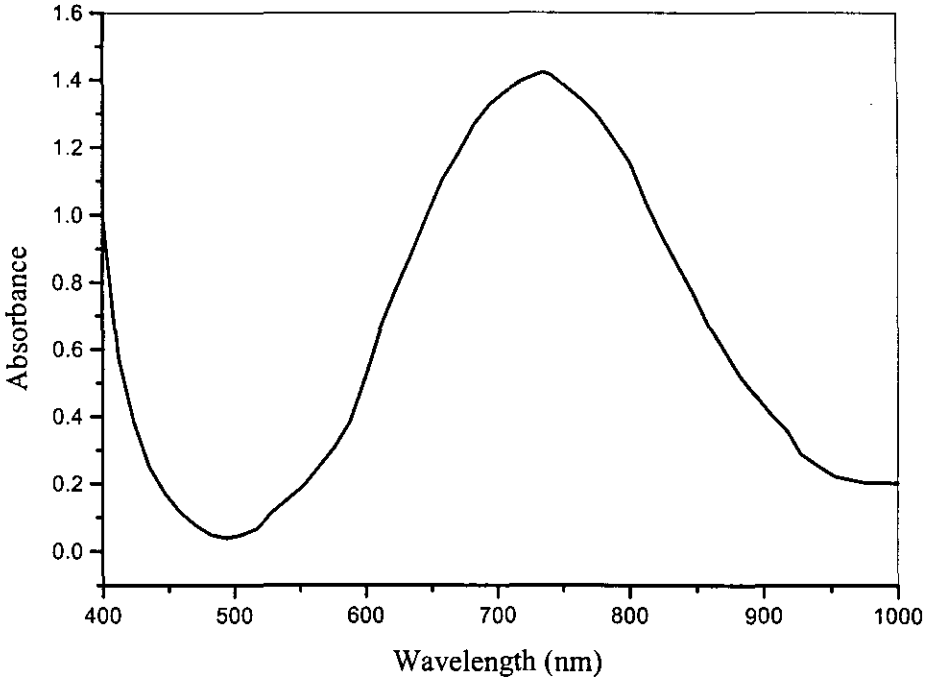


Figure 4.3 A typical absorption spectrum of the test solution having glucose concentration 4 gm/litre

The absorption spectra for the test liquids at various glucose concentrations are taken using a UV-Vis-NIR spectrophotometer (SHIMADZU Model No. UV - 160 A). A typical absorption spectrum of the experimental liquid at a glucose concentration of 4 gm/litre is given in figure 4.3.

It is observed that there is a shift (807 nm to 730 nm) towards the propagating wavelength (670 nm) for the maximum absorption wavelength of the test solution with glucose concentration. This enhances the EW absorption resulting in a change in output intensity. As the concentration increases, shift is found to increase. At higher concentrations, the graph shows a saturation. However, the device can be used for reliable measurements up to a glucose concentration of about 4 gm/litre. The evanescent absorbance A of the uncladded fibre is given as

$$A = \frac{r \alpha L}{2.303}$$

where 'r' is the fraction of the power outside the core, α is the bulk absorption coefficient of the surrounding medium and L is the length of the uncladded region of the fibre. This shows that for a fluid medium obeying Lambert-Beer law of absorption, evanescent absorbance depends linearly on the exposed fibre length, fluid concentration and the V parameter[28]. From our investigations we have found that variation of the output intensity at lower concentrations is linear to a fair approximation and at about 4 gm/litre, it shows saturation. Thus the plot can be divided into two portions, a linear region and a saturation region. This nonlinearity is due to the adsorption of the white precipitate on the fibre core, which is formed as a result of the reaction between Benedict's quantitative reagent with glucose solution on heating. Benedict's quantitative reagent contains potassium thiocyanate as well as copper sulfate and in the presence of the former a white precipitate of cuprous thiocyanate is formed on reduction by glucose. The small amount of potassium ferrocyanide in the quantitative reagent also aids in keeping cuprous oxide in solution.[62] As the concentration of glucose in the test solution increases, more and more quantity of Benedict's reagent is consumed in the chemical reaction with glucose, which in turn increases the amount of white precipitate produced.

Different groups have observed this nonlinear behaviour of the output light intensity with concentration of the fluid in the uncladded region.[23-25,38,48,73] Followed by our investigations on evanescent wave fibre optic sensor for the glucose concentration measurement, L M Bali et al developed an optical sensor based on monitoring the light scattered by the red particles of cuprous oxide produced as a result of the reaction between glucose and Benedict's qualitative reagent.[74] These investigations have also shown that there is a saturation at about 4 gm/litre for a test solution taken in the ratio 1:3. One of the limitations of using Benedict's qualitative reagent is that it can also be

reduced by many other reducing substances that are not carbohydrates, such as glucuronic acid, salcyluric acid, uric acid, creatinine and homogentisic acid etc.[62]

From our investigations, it is observed that the optimum ratio of glucose solution with Benedict's reagent is 1:3. Core of the fibre used for our sensor is made of silica and its surface is neutral having no net surface charge. When this uncladded fibre is immersed in aqueous solution of glucose, H^+ and OH^- ions as well as H_2O react with the surface to form an amphoteric hydroxylated layer on the surface of the silica core of the optical fibre.[73] The white precipitate formed due to the reaction between glucose solution and Benedict's reagent will experience considerable electrostatic attraction towards the silica core which leads to surface loading of the silica core and subsequent saturation of the output intensity.

Our fibre optic sensor system can be employed to monitor glucose concentration at low levels with good sensitivity. The dynamic range of the sensor can be varied by increasing the length of the uncladded region of the fibre. Even though a wide range of conventional and cheap methods are available for monitoring glucose in urine, their detection range is well above 0.2 gm/litre, which is the physiological limit.[62] The fibre optic sensor presented here with very high sensitivity at very low concentrations is ideally suited to monitor glucose even below this limit of 0.2 gm/litre. Also, the urine required for analysis can be kept small.

By making use of the advantages of the optical fibre sensing technology and the results obtained in our investigations, we have fabricated a hand-held device for the determination of glucose concentration. This FOS is made cost effective by using an LED instead of a laser diode and by replacing the photomultiplier tube by a photodiode. The block diagram of the hand-held fibre optic glucose sensor is presented in figure 4.4.

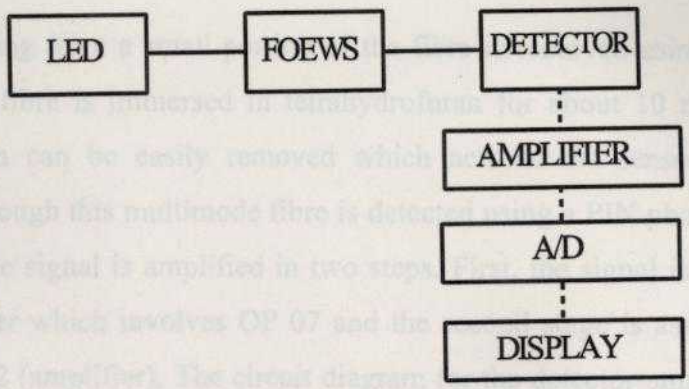


Figure 4.4 Block diagram of fibre optic glucose sensor

The photograph of the same is as shown in figure 4.5.

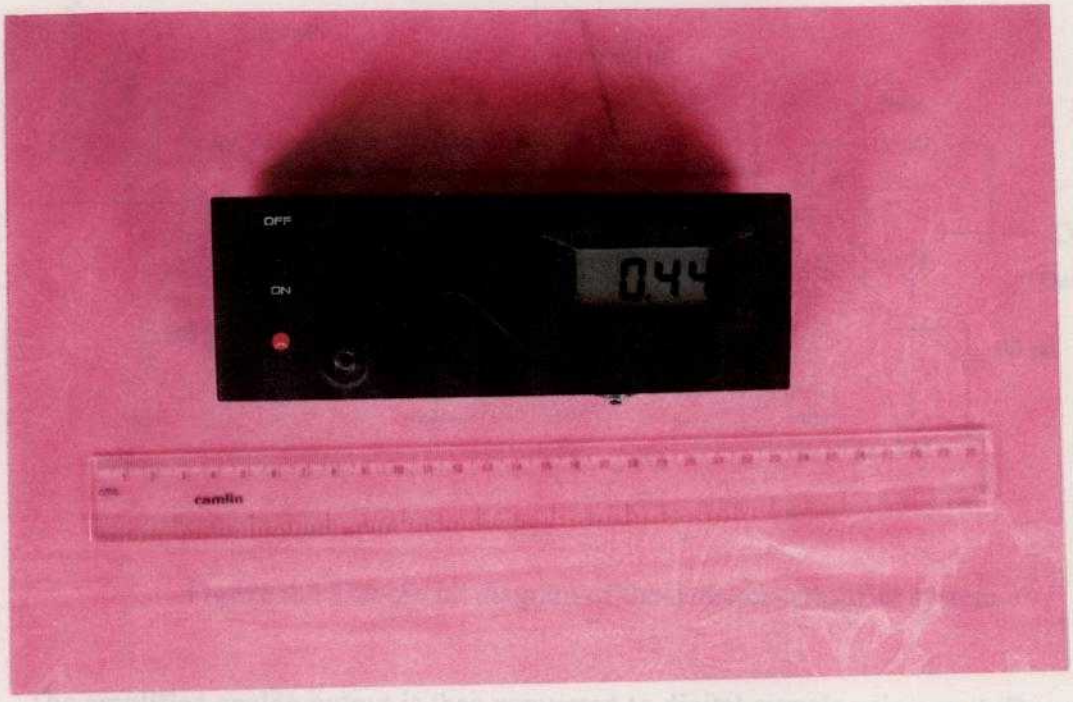


Figure 4.5 The photograph of the hand-held fibre optic glucose sensor. The dimension of the device is 178 mm X 62 mm X 46 mm

This device consists of a light emitting diode (LED) emitting at 820nm (Motorola MFOE 71) coupled to a multimode plastic fibre (1000 μm) and a photodiode.

Protective coating from a small portion of the fibre is removed using a blade and this portion of the fibre is immersed in tetrahydrofuran for about 10 minutes. Then this cladding region can be easily removed which acts as the sensor head. The light propagating through this multimode fibre is detected using a PIN photodiode (Motorola MFOD 71). The signal is amplified in two steps. First, the signal is amplified using a current amplifier which involves OP 07 and the second stage is assembled using two stages of TL072 (amplifier). The circuit diagram for the detector-amplifier system is as shown in figure 4.6.

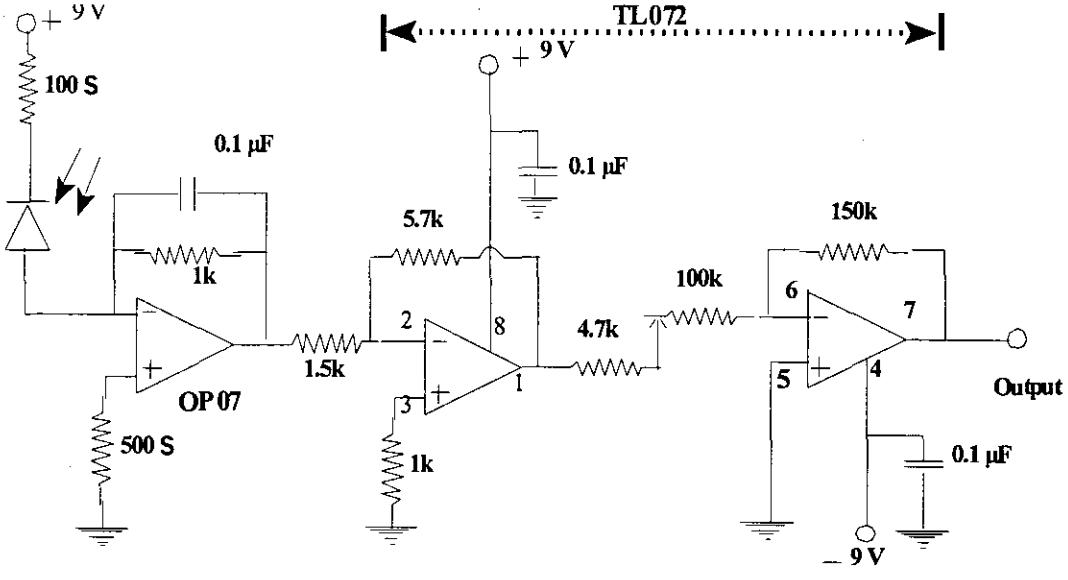
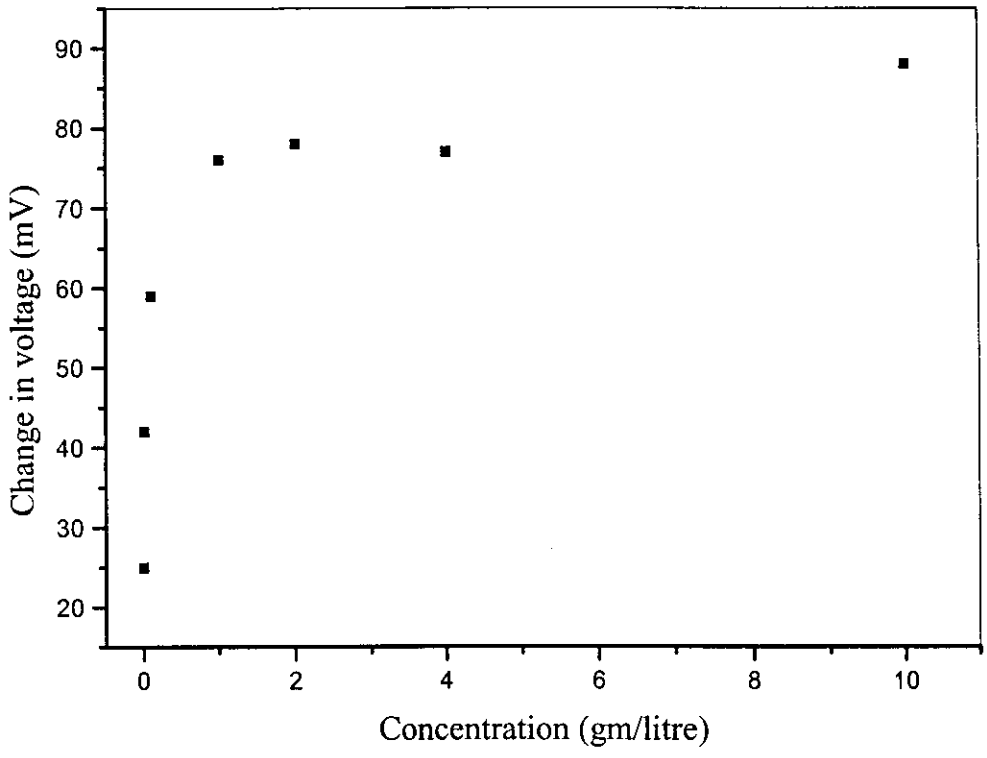
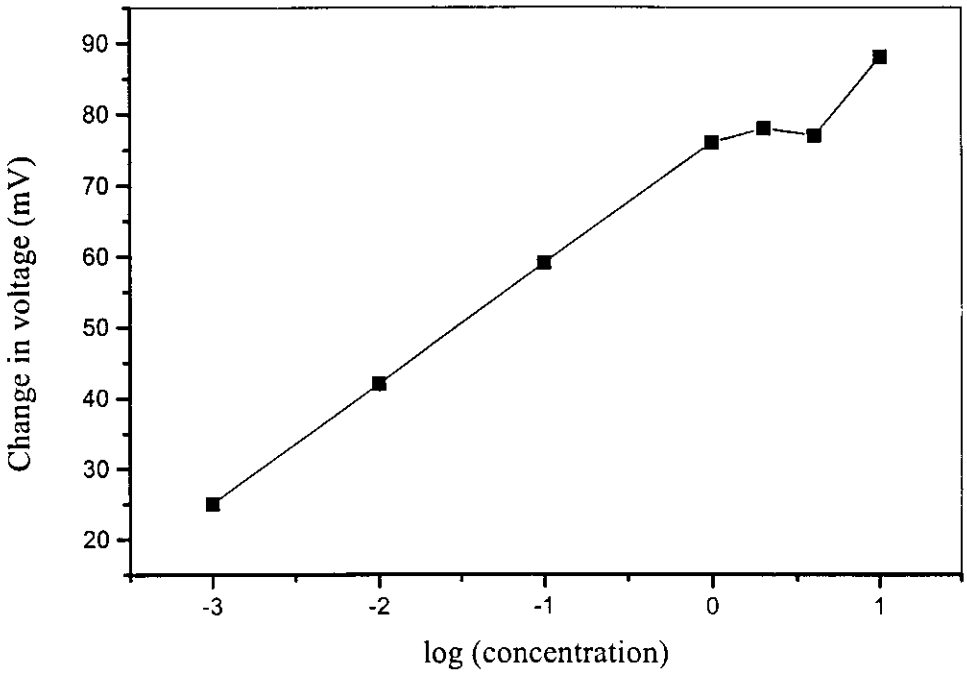


Figure 4.6 The circuit diagram of the detector-amplifier system

The amplified analog output is then converted to digital signals using an A/D converter and displayed on an LCD. Investigations carried out using this sensor have shown a linear response for low glucose concentrations. Measurements have also been carried out by replacing the LED by a laser diode emitting at 670nm (4.25 mW). The response obtained for different glucose concentrations is given in figure 4.7.



(a)



(b)

Figure 4.7 Response of the fibre optic sensor device (a) concentration vs. output voltage (b) log (concentration) vs. output voltage

4.4 Conclusion:

In this chapter we have discussed the design and development of an optical fibre based glucose sensor. It offers very good sensitivity at low glucose levels and its linear response region is very much within the physiological limit and hence can be used for the quantitative determination of glucose concentration in urine samples.

Even though it is inexpensive, there are a few drawbacks for this sensor. It needs heating of the test solution. Another disadvantage is the adsorption of the white precipitate on the fibre core formed as a result of the reaction of glucose solution with Benedict's reagent. This limits its application to disposable devices to measure glucose concentrations.

Chapter 5

EVANESCENT WAVE FIBRE OPTIC SENSOR TO DETECT NITROGEN DIOXIDE

Abstract

A novel method for the detection of pollutant and highly toxic nitrogen dioxide gas is described in this chapter. This fibre optic gas sensor works on the principle of evanescent wave absorption phenomenon. Here, an NO_2 sensitive material, metal phthalocyanine, incorporated along with an optical fibre acts as the sensing element. Investigations on the sensitivity of this device with different metal phthalocyanines were carried out and the reusability of the device was also verified.

5.1 Introduction:

The tri-atomic molecule NO_2 is a highly reactive gas and it combines with ambient oxygen to form mixture of various oxides of nitrogen. This toxic gas has a major contribution in the atmospheric pollution process. The presence of NO_2 in atmosphere is injurious to the plants, animals and human beings. It reduces the growth process of plants and enhances the illness rate of animals and human beings. Its affinity to water is the main cause for formation of acid rain. There are many different methods for the quantitative detection of nitrogen dioxide in a gaseous sample. Various NO_2 estimation techniques depend on photometric (absorption, fluorescence, etc), calorimetric, adsorption and chemiluminesence measurements.[75-80] Apart from these conventional techniques, recently a new method involving certain organometallic materials, viz. metal phthalocyanines, is coming up for the effective detection of NO_2 gas. The electrical, optical and mass addition properties of metal phthalocyanines have been utilised for the design of a class of NO_2 sensing devices.[81-93]

Metal phthalocyanines have attracted a great deal of attention for a long time because of their unique properties such as semiconductivity, photoconductivity etc. Another important feature of metal phthalocyanine is its chemical and thermal stability. As a result they have drawn attention in many potential applications like semiconductor devices,[94] optical data storage,[95] etc. Metal phthalocyanines exhibit large and fast nonresonant optical nonlinear response owing to the presence of delocalised two dimensional π electrons. Their nonlinear properties have been well investigated using techniques like degenerate fourwave mixing (DFWM), Z-scan etc.[96-99] Also phthalocyanines are good optical limiters as they show excited state absorption (ESA).[100-101] Apart from these, MPcs were extensively used in gas sensing applications. Due to their high sensitivity to NO_2 and their superior thermal and chemical stability, they offer good potentiality for NO_2 detection. Phthalocyanines allow incorporation of different metal atoms and a number of modifications can be achieved by substituting side groups in the molecular structure and thus we can influence its physical and chemical properties. Reversibility of this material makes them more attractive as a good gas sensing material. Also, many of these metal substituted phthalocyanines can be vacuum sublimed without much difficulties to give stable films and hence possess technological easiness to incorporate them in different sensing designs.

Many groups of workers have studied the electrical conductivity of metal phthalocyanines in the presence of NO_2 gas and developed different amperometric gas sensors based on MPc.[81-87] Since MPcs are p type organic semiconductors, they exhibit excellent sensitivity to electron acceptor gases such as NO_2 even at low concentrations. Gas adsorption on the surface of these MPc thin films follow charge transfer reactions which induce the generation of charge carriers and hence enhances the conductivity and in principle provides the basis for the development of a sensing system for NO_2. Though this technique has certain limitations, the possibility of using organic semiconducting materials for the sensing purpose is due to the following two reasons. One thing is that the electrical conductivity of organic semiconductors can change by many orders of magnitude when a gas adsorbs on their surface, which make them ideal for detecting very low concentrations of pollutants. The second thing is that the organic molecules

may be structurally modified which may increase their selectivity to particular gaseous species. We can find from the literature that a variety of metal substituted phthalocyanines were studied for NO_2 detection by different researchers by exploiting its electrical conductivity property. A Krier et al studied the electrical behaviour of Chloro-Aluminium-Phthalocyanine (ClAlPc) thin films in the presence of NO_2.[87] They measured the changes in the dark conductivity of these films on exposure to NO_2 gas at different temperatures. S Dogo et al have reported their results on the electrical conductivity studies of copper phthalocyanine (CuPc) thin film in the presence of NO_2.[81] C Haman et al have analysed the NO_2 sensitivity on monoclinic and triclinic modifications of lead phthalocyanines.[82] Y Sadaoka et al investigated the influence of the changes in topography and structure of film on the electrical properties of MPc film and also on the sensitivity of the same to NO_2 gas.[84]

Another widely accepted method of detection of NO_2 is by using Quartz Crystal Microbalance (QCM).[92-93] This is achieved by forming either Langmuir-Blodgett (LB) films or thin films of MPc on a quartz crystal microbalance, which is oscillating at a particular frequency. NO_2, an electron acceptor gas, forms a donor-acceptor complex with MPc and the resulting mass increase can be measured by the frequency shift of the QCM. Thus sensing principle of QCM is the mass loading by adsorption of NO_2 on the MPc surface and the resulting change in the oscillation frequency. S R Kim et al synthesised a bulky alkyl-group-substituted MPc and stacked it as a LB multilayer on a QCM. They measured the adsorption capacity of NO_2 by different metal substituted phthalocyanines.[92] A complete regeneration of the sensor is not possible in this method. It is observed that prolonged heat treatment at elevated temperatures gave some recovery. But in the repeated adsorption tests of NO_2, the sensor could not reproduce its initial frequency change satisfactorily. This is one of the major limitations of this method.

Surface Plasmon Resonance (SPR) technique is another approach utilising MPc for the detection of NO_2.[90,102] Very thin layers of metallophthalocyanines are used in this technique for the detection of NO_2, which is formed on a thin metal layer. In this

case, the change in the optical properties of the active layer in response to external ambients are measured by monitoring the coupling of photons to surface plasmons at the interface between a metal and an active layer. There will be a shift in the SPR curve to higher angles on exposure to NO_2 and also we can see a small decrease in the depth of the SPR curve. The effect is partially reversible although the time required is very large.

The optical properties of metal substituted phthalocyanines in an NO_2 environment forms one of the major parametric studies undertaken by different research groups.[88-91] D Campbell et al conducted electrical conductivity and optical absorption studies simulatneously for lead phthalocyanines (PbPc) thin films exposed to NO_2.[86] In another paper D Campbell et al investigated the spectral response of monoclinic and triclinic phases of PbPc thin films in the presence of NO_2.[91] They observed that visible and IR spectra of both phases are significantly affected by the presence of NO_2.

The above mentioned methods have numerous disadvantages and limitations. In amperometric NO_2 sensors, the detected signal is affected by electromagnetic as well as radio frequency interference. The regeneration possibility of this device is very poor and the signal response is also influenced by temperature. In the case of quartz crystal microbalance (QCM), a complete regeneration of the sensor is not possible. Repeated adsorption tests of this device limits its reproducibility.

In the coming sections, we discuss a novel method for NO_2 detection that eliminates most of the difficulties and disadvantages of the conventional techniques.

5.2 Optical fibre based sensor design:

An optical fibre based NO_2 sensing system is designed and fabricated during the course of our investigation. In this fibre optic sensor, we have incorporated metallophthalocyanines into a multimode cylindrical waveguide structure by replacing a portion of the cladding region. A uniform coating of highly purified MPc is deposited

by thermal evapoartion at a reduced pressure of the order of 10^{-5}mbar. The structure of the sensor element is as shown in figure 5.1.

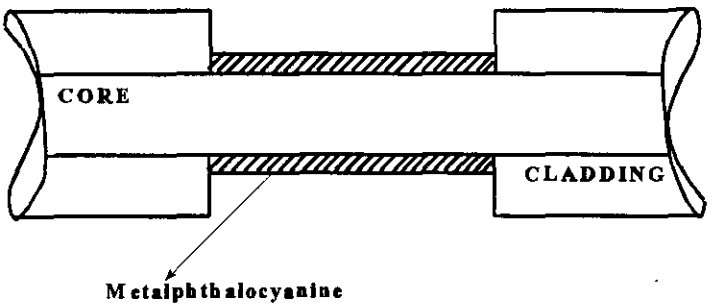


Figure 5.1 The structure of the fibre optic gas sensor element

Metal substituted phthalocyanines are widely accepted for their strong affinity to nitrogen dioxide and optical absorption behaviour at NO_2 atmosphere. Here, in the fibre optic sensor, the evanescent waves at the sensor region get affected by the change in the optical property of the MPc cladding in the presence of NO_2 gas. This is utilised for the characterisation of this novel optical fibre sensor design. Besides its simple structure, this fibre optic NO_2 sensing device offers numerous advantages. Using this sensor it is possible for in-situ detection of NO_2, which is highly useful in mines and industries. These evanescent wave fibre optic sensors are also immune to electromagnetic interference, possess multiplexing capability etc.

5.3 Experimental details:

The schematic of the experimental set-up is as shown in figure 5.2. Light from a diode laser emitting at 670 nm (4.25 mW) is focussed at one end of a multimode plastic clad silica fibre (200/380 μm) and the guided waves are detected using a fibre optic powermeter (Meggar OTP 510) at the other end of the fibre. The sensor head is placed in a chamber that can be evacuated to lower pressures. Nitrogen dioxide gas is allowed to flow through an inlet port provided in the chamber. The investigations have been carried out for different NO_2 gas concentrations in the chamber that is evacuated to

rotary vacuum (10^{-3} mbar) and by employing different metal substituted phthalocyanine at the sensor head.

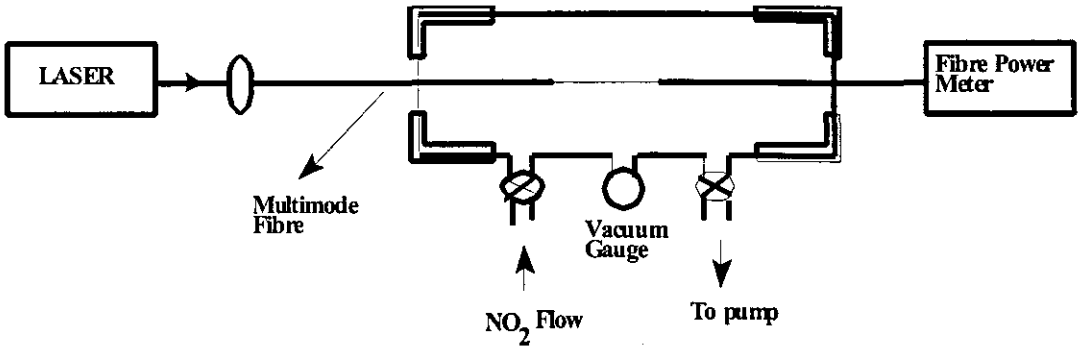


Figure 5.2 Schematic of the experimental set-up for the nitrogen dioxide detection

A length of 0.04 m of the cladding of the multimode plastic clad silica fibre is replaced with uniform coating of a metal phthlocyanine. The thickness of the MPc coating is about 140 nm. The structure of the MPc is as shown in figure 5.3 and its synthesis and purification procedures are discussed elsewhere.[103]

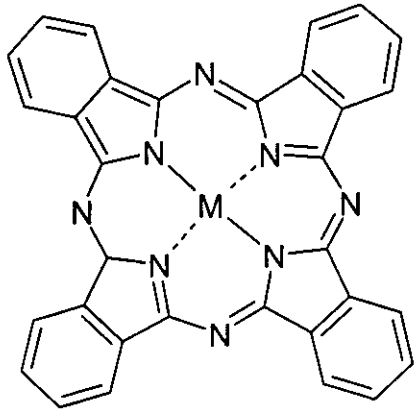


Figure 5.3 Molecular structure of the metal phthalocyanine. M – Cu, Pb

We have carried out experiments with different metal substituted phthalocyanines as the sensor element. Investigations have been carried out with Copper phthalocyanine (CuPc), Lead phthlocyanine (PbPc) and Samarium diphthalocyanine (SmPc) coated at the uncladded region of the fibre to form efficient gas sensing system for the detection of NO_2 gas.

5.3.1 FOS with CuPc sensing element:

Copper phthalocyanine shows very good affinity to NO_2 and it provides a very rapid response. The absorption spectrum of CuPc thin film is as shown in figure 5.4(a) and the peak wavelengths are at 620 nm and at 697 nm.

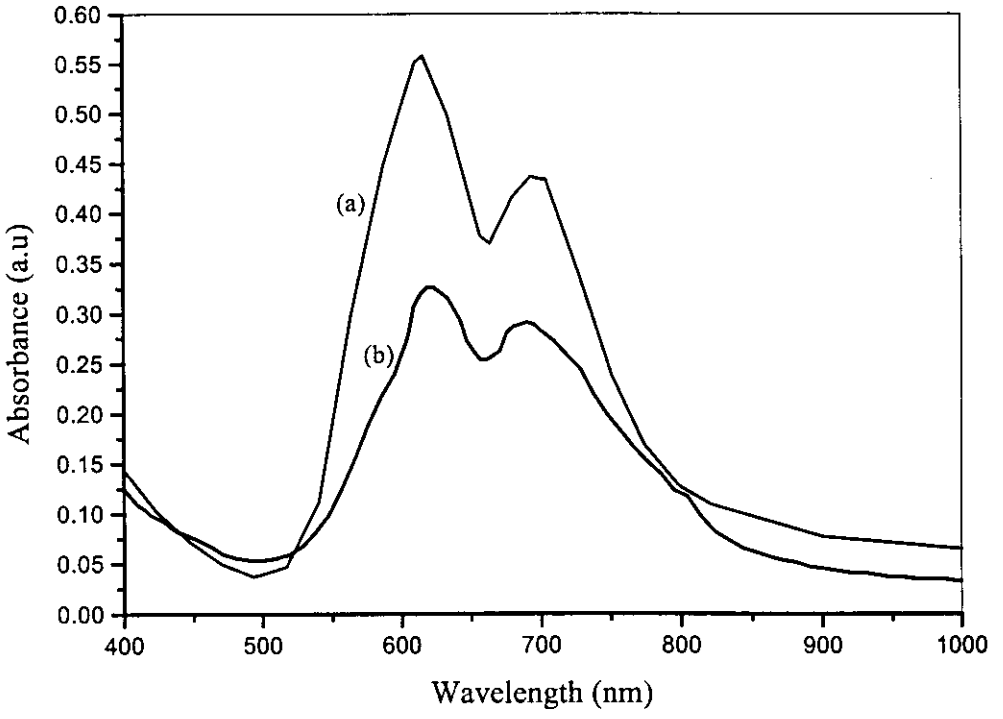


Figure 5.4 Absorption spectrum of Copper phthalocyanine thin film shows blue shift after exposure to NO_2 gas. (a) Spectrum before NO_2 exposure (b) Spectrum after NO_2 exposure

The flow of NO_2 gas through the sensor chamber is maintained steady and the interrogating wavelength is 670 nm from a 4.25 mW diode laser. As soon as NO_2 molecules reach the sensor element, it gets adsorbed on the surface of the MPc. Adsorption of NO_2 molecules on CuPc leads to a decrease in intensity and a shift in the 697 nm absorption peak towards 670 nm. This leads to a variation of the output power through the fibre due to change in the evanescent wave absorption. At the interface of the SiO_2 core and CuPc cladding in the sensor region, attenuated total internal reflection (ATR) takes place. The variation of the output power with time for this sensor is given in figure 5.5.

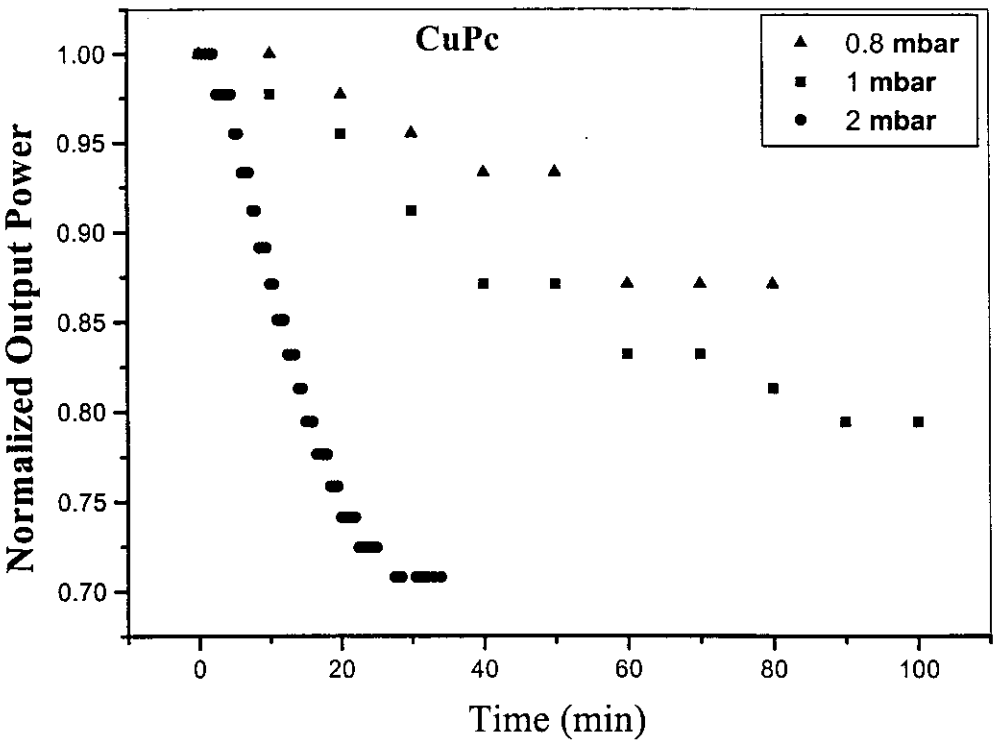


Figure 5. 5 Variation of the output power with time for CuPc coated fibre optic sensor at three different concentrations of NO_2

The plots show the sensor response to three different nitrogen dioxide concentrations. The variation of output is attributed to the blue shift in the absorption peak of CuPc on NO_2 adsorption (figure 5.4). S R Kim et al observed a similar shift for the CuPc

Langmuir-Blodget film exposed to NO_2 gas. They found that the strong absorbance at 690 nm and at 630nm decreased in intensity and new absorbance at 580 nm appeared. These changes are characteristic of the formation of MPc radical cation.[92] D Campbell et al in their paper studied the spectral response of monoclinic and triclinic lead phthalocyanines in the presence of NO_2.[91] In the NO_2 environment, they have also observed a decrease in intensity of the absorption peak.

5.3.2 FOS with PbPc sensing element:

Different groups have carried out extensive research on electrical and optical properties of lead phthalocyanine (PbPc) thin films in the presence of NO_2 gas.[82-84,86,88,89] In our investigation, we have examined the role and characteristics of PbPc in the optical fibre sensor design.

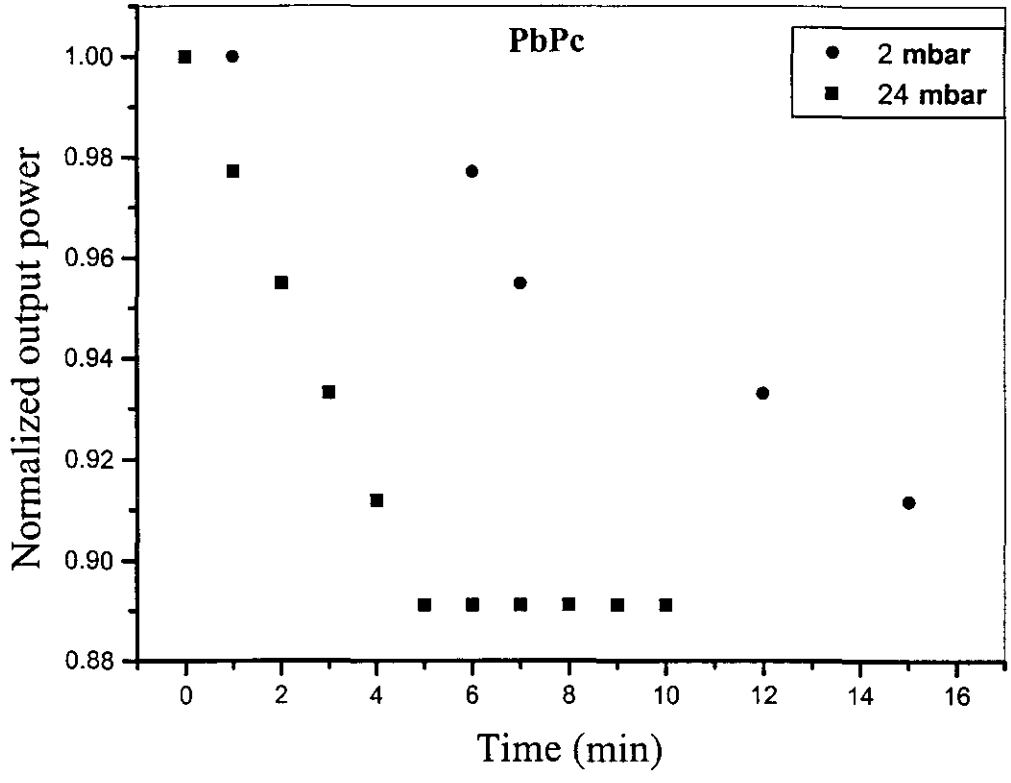


Figure 5.6 Variation of the output power with time for lead phthalocyanine coated fibre optic sensor at two different NO_2 concentrations.

The variation of the output power of the light propagating in the fibre optic sensor system with time using PbPc thin film coating on the sensor element is as shown in figure 5.6 The plot clearly reveals the NO_2 affinity of lead phthalocyanine deposited on the sensor region and the response of the device at two different gas concentrations. It is observed that the variation is small at low concentrations of NO_2. At higher concentrations, fast response followed by a satutration behaviour is observed.

5.3.3 FOS with SmPc sensing element:

We have also characterised the Samarium diphthalocyanine coated evanescent wave fibre optic sensor for NO_2 detection during the course of our investigations. SmPc has a sandwich structure as shown in figure 5.7 and shows very good response to NO_2 gas. Two phthalocyanine clouds sandwich samarium atom and hence it is influenced by higher π electron contribution.

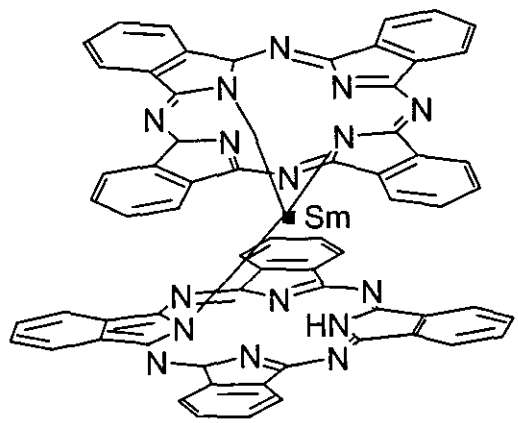


Figure 5.7 Molecular structure of Samarium diphthlocyanine

A uniform coating of SmPc is deposited on the uncladded region of a multimode optical fibre by thermal evaporation procedure under reduced pressure. The absorption peak of SmPc thin film is at 653 nm and in the NO_2 environment (2 mbar) the peak shifts to 679 nm as shown in figure 5.8.

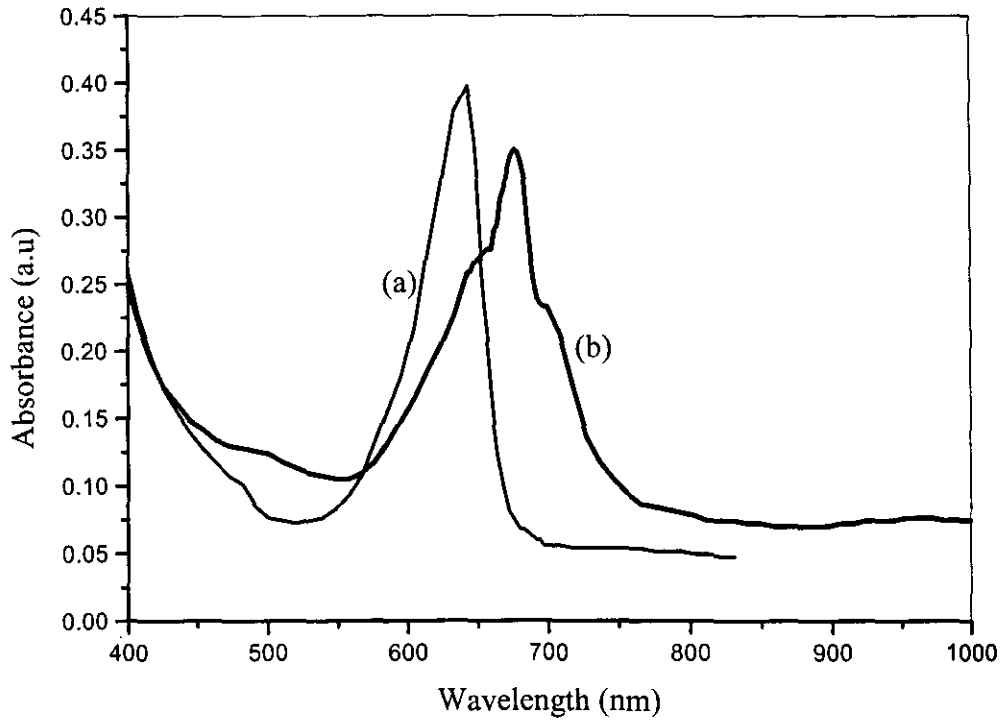


Figure 5.8 The spectral response of Samarium diphthalocyanine (a) Before NO_2 exposure (b) After NO_2 exposure

This spectral response has been exploited in the design of an evanescent wave fibre optic sensor. The response of this SmPc coated fibre optic evanescent wave sensor is observed for three different NO_2 environments and the variation of the output power with time is recorded and analysed. The output power variation with time at different NO_2 concentrations is as shown in figure 5.9. Even in this case the response is faster at higher concentrations.

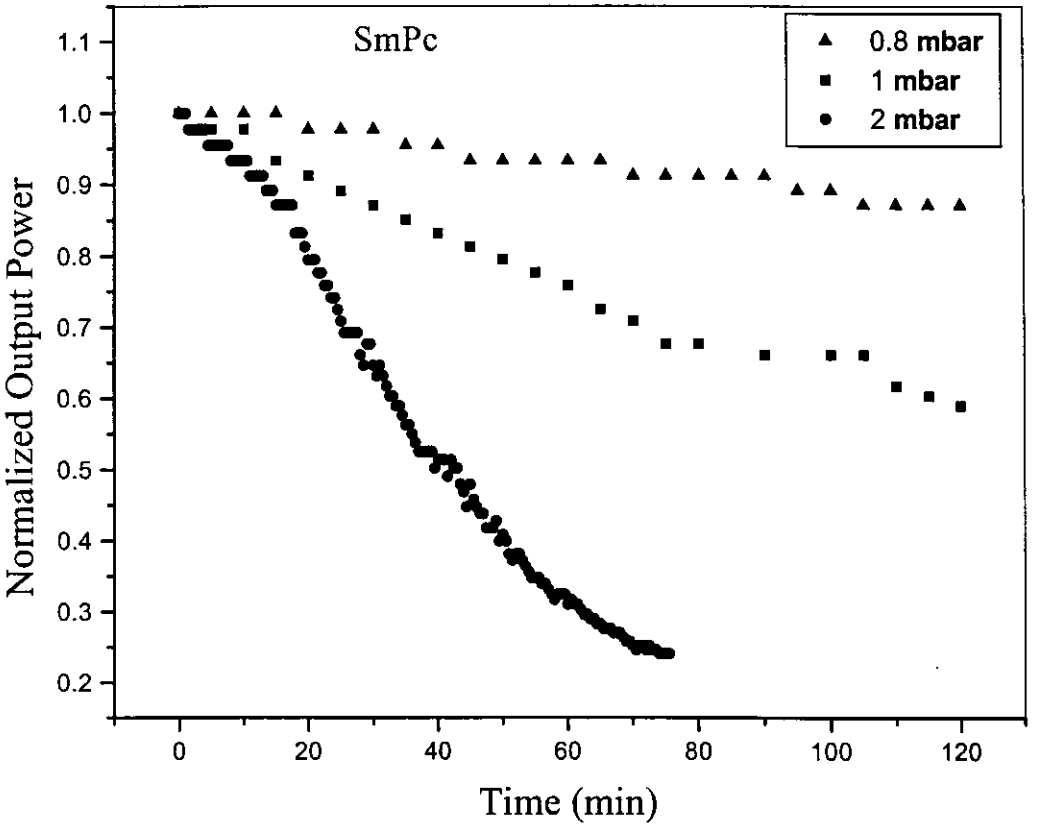


Figure 5.9 Variation of the output power with time for SmPc coated fibre optic sensor at three different NO_2 concentrations

S R Kim et al have investigated the regeneration capability of NO_2 sensors based on quartz crystal microbalance (QCM) by forming mono and multilayer LB films of Metallophthalocyanines.[92] At room temperature they have observed that the regeneration of the sensor is not satisfactory. But satisfactory regeneration was found when QCM was treated in vacuum at 170^0C for 30 minutes. We have also checked the SmPc coated fibre optic sensor for its regeneration capability. This is achieved by helically winding a kandal wire across the sensor head and applying an ac voltage across it. The temperature ($\approx 140^0$C) was measured at the sensing region using a thermocouple. The reversibility of the sensor is illustrated in figure 5.10. It has been observed that the response of the device keeps on changing on repeated regeneration trials. It was also seen that the response becomes faster after repeated NO_2 exposures

and subsequent heating. This suggests that the method adopted for regeneration is not completely satisfactory.

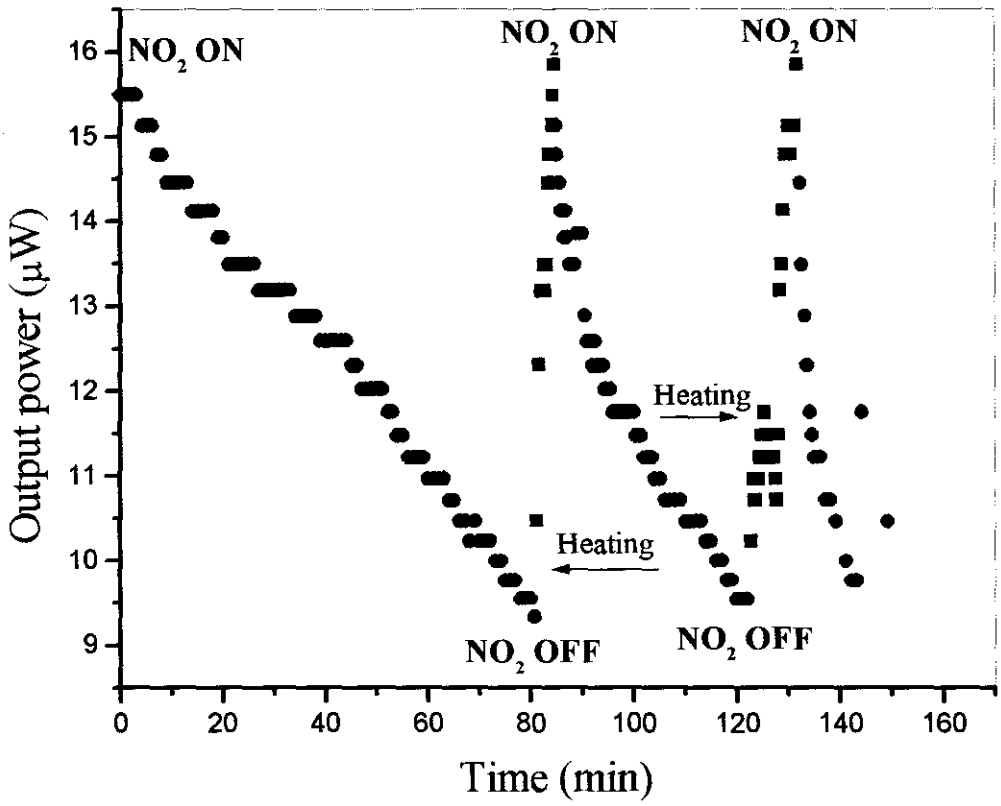


Figure 5.10 Plot showing the response of Samarium diphthalocyanine coated fibre optic sensor under repeated NO_2 exposure and heating.

5.4 Comparative analysis:

S R Kim et al investigated the NO_2 response of different metal substituted phthalocyanines, which are stacked in a multilayered form on a quartz crystal microbalance (QCM) by Lagmuir–Blodgett (LB) method.[92] They tried with four different phthalocyanines like H_2Pc, PbPc, CuPc, and CoPc. They found that the central metal atom has a profound effect on the response pattern, rate of adsorption of NO_2 molecule, adsorption capacity and adsorption kinetics. We have also carried out a comparison of the response of the fibre optic sensors developed using PbPc, CuPc and SmPc. Figure 5.11 shows the variation of the output power with time in the case of

these three sensors carried out at a pressure of 2 mbar NO_2 environment. Even though the response of these devices remain more or less the same, it is seen that the fibre optic sensor system using SmPc gets saturated only after prolonged exposure to NO_2. This suggests that SmPc has a greater capacity to adsorb NO_2. Reversibility of the sensor was tried in the case of CuPc and SmPc. It was seen that CuPc does not get regenerated back to its initial condition on heating ($\approx 140^0$C) whereas SmPc exhibits partial recovery.

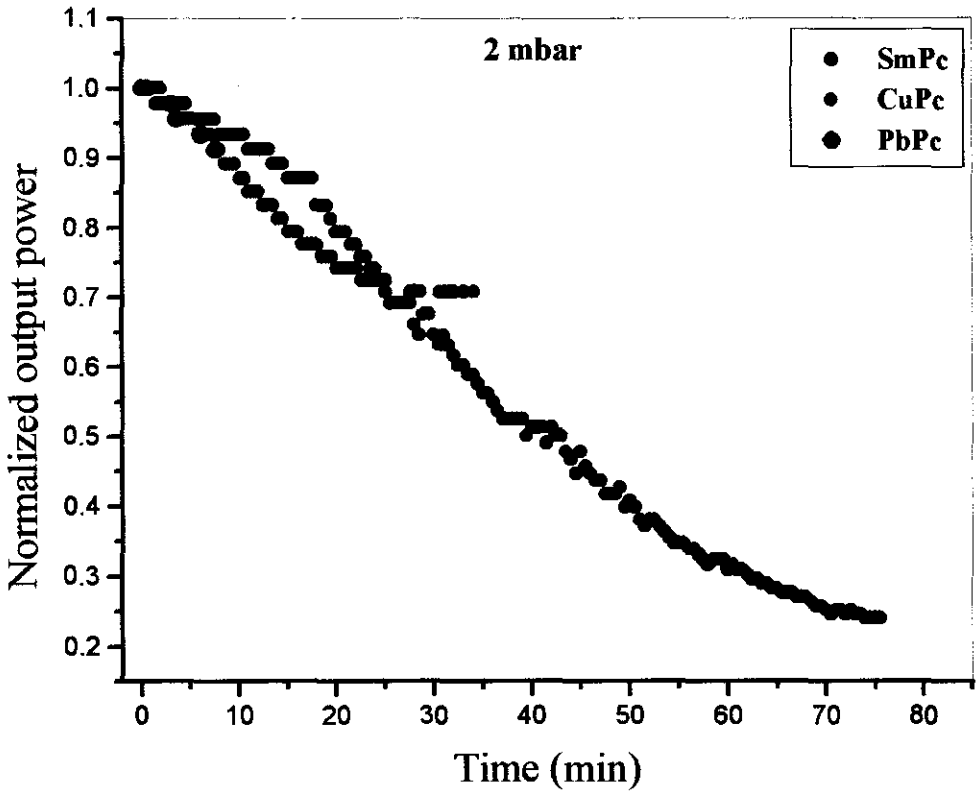


Figure 5.12 Variation of the output power with time for three different metal phthlocyanine-coated optical fibre sensors at an NO_2 concentration of 2 mbar.

5.5 Conclusion:

We have designed and developed a new technique based on evanescent wave absorption in optical fibre for the NO_2 detection using MPc. It was observed that effective and

sensitive detection of NO_2 can be done by this method. It has been established that the response of fibre optic sensors developed using SmPc, PbPc and CuPc shows more or less similar response. But, fibre optic sensors based on SmPc exhibit saturation only after prolonged exposure to NO_2. Even though SmPc based sensor exhibits regenerative capability, the performance is not fully satisfactory.

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