Development of a fiber optic chemical sensor for detection of toxic vapors

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This work is dedicated to my Parents, Chandravati Bansal and Mulchand Bansal and my sister Anita, who have provided me with endless love, support and encouragement.
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Abstract

Development of a Fiber Optic Chemical Sensor for Detection of Toxic Vapors
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Nerve agents are among the most potent of the chemical warfare agents being highly toxic in both liquid and gaseous form. In this thesis the development of a fiber optic chemical sensor for detection of organophosphorous nerve agent sarin precursor dimethyl-methylphosphonate (DMMP) is presented. The optical fiber sensor developed is based on the modified cladding approach using conducting polymer polypyrrole as a chemo-chromic material. Polypyrrole is synthesized by chemical oxidation and characterized by FTIR and Raman Spectroscopy. To characterize the electrical and optical property changes that come about in polypyrrole upon exposure to DMMP, four probe technique, ellipsometry, thin film transmission are used.

The polypyrrole coating is applied to un-cladded fiber core using two different coating techniques, i.e. in-situ deposition and monomer vapor phase deposition. Preliminary results show an intensity decrease of 2.1% when the sensing element is exposed to 134ppm of DMMP. Three different dopant anions, i.e. 1-5, Naphthalene disulphonic acid, Anthraquinone sulphonic acid and Hydrochloric acid, are added to improve the sensor sensitivity. The developed device is tested for DMMP sensitivity optimizations in terms of substrate nature, Cu²⁺ dopant, waveguide geometry, and light source intensity. The sensitivity optimization has resulted in a 25.75% sensor response and a detection of 26ppm of DMMP concentration. Selectivity and environmental stability of the developed device is investigated. The mechanical property and adhesion investigated using the nanoindentation and ASTM D - 4541 pull-off test method. The influence of these adhesion enhancements on the sensor response is investigated.
CHAPTER 1: INTRODUCTION

Chemical and biological warfare agents pose a growing threat to national security. One of the major steps toward controlling this problem is to develop sensor devices that can act as an early warning system to the endangered personnel. Nerve agents are chemicals that attack the central nervous system. A release of a nerve agent has the potential to rapidly affect a large number of people. The majority of nerve agents belong to a class of compounds called Organophosphates. Dimethyl methylphosphonate (DMMP) (98% pure) is nominated by the U.S Army for toxicology and carcinogenesis studies. This is because it is being considered for use to stimulate the physical and spectroscopic properties of anticholinesterase (nerve) agents. When a nerve receives a stimulus acetylcholine is released in order to carry the impulse to muscles and organs. Once the impulse has passed the enzyme cholinesterase acts to prevent the accumulation of acetylcholine after its release in the nervous system. Nerve agents inhibit the functioning of cholinesterase as a consequence of which the acetylcholine continues to act so that the nervous impulses keep on being transmitted [1]. The acute effects include nausea, diarrhea, inability to perform simple mental tasks and respiratory effects for a moderate exposure [2]. Therefore, the development of an early warning system, based on detection of toxic materials, is now an important topic for research and development.

Fiber optic sensor systems provide with numerous advantages over conventional systems which include immunity to electromagnetic interference, small and compact size, sensitivity, ability to be multiplexed, remote sensing and the most
important of which is the ability to be embedded into textile structure[3]. An optical fiber forms an effective medium to sense chemical species. The presence of chemical species can modulate light property such as intensity, phase or polarization in the optical fiber. These changes can be detected at the fiber output and can be related to the concentration of the chemical species present at the point. Sensing of chemical agents using fiber optic sensor systems has been reported in literature for 50 – 60 years [4]. These include sensors for toxic chemicals such as ammonia, hydrazine, hydrogen peroxide, organophosphate nerve agents [5][6]. The optical fiber can actively take part in the sensing mechanism i.e. the optical fiber structure is modified for sensing function. This type of sensor is termed as intrinsic optical fiber sensor. The optical fiber can also serve as a mere light guiding element to an external transducer, this type of sensor is termed as extrinsic optical fiber sensor. From sensitivity and selectivity point of view, for the work in this thesis, we choose to develop an intrinsic type sensor to sense DMMP.

The optical fiber itself is not reactive to the presence of DMMP since the light is guided into the core of the optical fiber with a very small amount penetrating in the cladding as evanescent field not accessible to DMMP. The structure of the optical fiber needs to be modified in such a way that the presence of DMMP can modulate light property into the fiber core. This is done by removing the cladding of the optical fiber and coating this section with a DMMP sensitive material. This type of sensor design is referred to as modified cladding or coating design for optical fiber sensors. The sensitive material (referred to as modified cladding) is chosen in such a way that
the presence of DMMP can change the optical properties of the sensitive material. This optical property change brings about a change in the evanescent field in the modified cladding bringing about a change in the intensity of light in the core of the optical fiber.

Conducting polymer polypyrrole is reported [7] to undergo change in conductivity when exposed to DMMP. This conductivity change is attributed to the change in hole concentration and mobility in the polypyrrole backbone due to DMMP exposure. This conductivity change leads to a refractive index change in polypyrrole upon exposure to DMMP. Hence polypyrrole can act as a sensitive material towards DMMP and can be applied to optical fibers as a modified cladding. Apart from its sensitivity towards DMMP polypyrrole possesses many other favorable properties which include: ease of processibility to form thin films on fiber, which forms the modified cladding and excellent ambient stability of the material, which does not lead to random fluctuations in sensor signal due to slight perturbations in the environment.

This thesis consists of seven chapters, following the introduction to the work in the thesis, chapter 2 covers the current state of art of optical fibers in chemical sensing and provides a literature review on fiber optic chemical sensors.

Chapter 3 describes the structure and light propagating principles of the optical fiber. The various general components and choice of a conventional fiber optic system is discussed. And the modified cladding design for optical fiber sensor,
which is used in the development of the chemical sensor presented in this thesis, is discussed in detail.

The modified cladding, i.e. conducting polymer polypyrrole, provides with an excellent class of materials for sensor applications. Chapter 4 begins with explaining the structure and properties of polypyrrole, and how it can be applied to sensor applications. The conductivity and workfunction modulation brought about in polypyrrole thin films due to interactions with gaseous species is discussed. Polypyrrole is synthesized in form of thin films using in-situ and monomer vapor phase deposition. The deposited polymers are characterized using FTIR and Raman spectroscopy and results of successful synthesis reported. The DMMP sensing property of polypyrrole films is measured using four probe technique to measure the change in resistivity of polypyrrole films when exposed to DMMP. The complex refractive index change in polypyrrole films is measured using ellipsometry for real part of refractive index and thin film transmission experiment for complex part. Chapter 4 reports successful synthesis and successful DMMP sensing using polypyrrole films.

Chapter 5 describes the process by which the sensitive polypyrrole film is applied to the fiber to realize an on-fiber sensor device for DMMP sensing. The fabrication process of the sensor device is a three step process which involves (a) etching a small section of the optical fiber to expose the core, (b) coating the etched section of the optical fiber with the polymer polypyrrole, (c) integration of sensor components i.e. laser-fiber-detector setup and testing. The preliminary developed
sensor shows a very limited sensor response of 2-3 %. The sensor sensitivity issue is investigated by changing the processing parameters and materials structures, such as doping the polymer material, changing the polymer microstructure by changing the processing technique, substrate nature i.e. hydrophilic or hydrophobic, sensing element diameter and length and light intensity. The best polymer dopant, processing technique and substrate nature are selected and sensitivity towards lower concentrations of DMMP is tested. Chapter 5 also reports experiments conducted on thermal and environmental stability and aging studies conducted on the sensor.

Poor mechanical properties of conducting polymers have been a serious issue in their applications in sensor devices. This part is addressed in chapter 6, in this chapter the mechanical property of the polypyrrole film is measured using the nanoindentation technique and compared to literature data. The adhesion between the polypyrrole thin film and glass substrate is measured using the ASTM 4541 pull off test and the adhesion between the glass slide and polymer thin film is enhanced by adding a silane coupling agent to the glass substrate prior to film deposition and increasing the roughness of the glass substrate prior to film deposition. These adhesion enhancement techniques are then applied to the fiber surface prior to thin film deposition and DMMP sensitivity test is conducted to report the influence of the fiber surface modification on the sensor response.

The conclusions drawn from the research and recommendations for future work are presented in chapter 7.
CHAPTER 2: FIBER OPTIC CHEMICAL SENSORS A LITERATURE REVIEW

2.1 Introduction

Optical measurement techniques have been used for about a century, although these techniques had been limited to laboratory making use of large optical tables which are required to maintain precise alignment between various optical components. This scenario has changed considerably due to the current revolution beginning in the 1970’s in optical sensing brought about by the development of low loss optical waveguides for telecommunications industry. These waveguides acted as an optical link between the light, source and the detector, solving the alignment issue to a great extent. Increased interest and effort in the area of telecommunications industries in the 1980’s resulted in a considerable decrease in the cost of expensive components such as lasers, detectors and couplers further fueling the fiber optic sensor research. Optical fiber sensors have been applied to monitor physical parameters such as temperature and pressure, but lately people have realized their potential in the area of chemical and biological sensing. This chapter presents the basics of optical fiber sensing along with how the structure of the optical fiber can be modified for sensing applications. A brief review on fiber optic sensors with special emphasis on chemical sensors is presented.

2.2 Fiber Optic Chemical Sensors

Use of optical fibers to sense chemical concentration has been reported in literature since 1946. The optical fiber sensors have since then found applications in chemical [8-11], biochemical [12-15], biomedical and environmental [16-19] sensing. In general optical fiber sensors are classified as intrinsic and extrinsic type. In the extrinsic type of sensor shown in Fig. 2.1a, the optical fiber is only used as a means of light
transport to an external sensing system i.e. the fiber structure is not modified in any way for the sensing function.

![Diagram](image)

(a)

![Diagram](image)

(b)

Fig. 2.1 Schematic showing the general design scheme of (a) intrinsic & (b) extrinsic optical fiber sensors.

Examples of extrinsic fiber optic sensors include fibers terminated in active layers e.g. optode [20], fibers having end face mirrors or fibers confronting other transducer elements or fibers [21]. The intrinsic fiber optic sensor differs form extrinsic sensors, where light does not have to leave the optical fiber to perform the sensing function. In the intrinsic fiber optic sensors the optical fiber structure is modified and the fiber itself plays an active role in the sensing function. Examples of intrinsic fiber sensors include, fibers with Bragg gratings, modified claddings or micro or macrobends, as shown in Fig.2.1b.
2.2.1 Extrinsic fiber optic chemical sensors: Optode

The basic optode design consists of a source fiber and a receiver fiber connected to a third optical fiber by a special connector as shown in Fig. 2.2. The tip of the third fiber is coated with a sensitive material, mostly by the dip coating procedure. The chemical to be sensed may interact with the sensitive tip by changing the absorption, reflection, scattering properties, change in luminescence intensity, change in refractive index or a change in polarization behavior, hence changing the reflected light properties. The fiber in this case acts as a light pipe transporting light to and from the sensing region.

![Fig. 2.2 Fiber Optic optode for chemical sensing.](image)

An example of an oxygen sensing micro-optode is shown in Fig. 2.3, the measurement principle of oxygen is that of collisional quenching of luminescence by oxygen. The luminescent indicators used are either fluorescent dies, like transition metal complexes [22] or phosphorescent dyes like platinum or palladium porphyrins [23]. The process of dynamic quenching of luminescence by oxygen changes the absolute emitted luminescence as well as the decay or life time of the luminophore. The optrode design is also used in bio-sensing to recognize molecules immobilized at the distal tip of optical fiber [12]. The change in optical properties which are brought about by the binding of the
analyte to the optrode tip are transmitted through the fiber to the detector, these are generally fluorescent signals.

Fig. 2.3 Portable oxygen micro-optode in a syringe casing (a) complete syringe, arrow points to protruded fiber tip; (b) tapered tip of oxygen micro-optode protruding out of the needle.

The main problem associated with this design is that the area of interaction between the chemical and the material is very small i.e. 8-10 microns in diameter, in the case of single mode fiber and 50-200 microns in diameter, in the case of multi mode fiber, which directly affects the sensitivity achieved from this type of sensors. To circumvent this limited sensitivity issue, these biosensors utilize a porous polymer or a semipermeable membrane or even porous beads which contain the recognition molecules
as shown in Fig. 2.4. This provides with an increased surface area available for reaction with the analyte, enhancing the sensitivity of the design.

2.2.2 Intrinsic fiber optic chemical sensors

There are four general sensor designs for intrinsic fiber optic chemical sensors, (a) fiber refractometer, (b) evanescent spectroscopic, (c) active coating, (d) active core. Each of these designs is dealt with, in detail in the following sections.

a. Fiber refractometer

The fiber refractometer is shown in Fig. 2.5, in this design the core of the optical fiber is exposed and the fiber is bent in a U shape. The presence of the analyte in the vicinity of the bend causes a change in the refractive index of the surrounding which changes the bend losses through the optical fiber causing a change in the transmission efficiency through the optical fiber. The application of this design is mainly in liquid level sensing.
small air bubbles in liquid can also be detected by this design, so this technique can also be applied to detect air leaks in pipe lines. Takeo and Hatori demonstrate the use of this design to measure the moisture content in the human skin and hence monitor dermatological health. This is done by pressing the refractometer onto the human skin, the device is then able to measure the moisture content in the skin. A straight stripped-fiber refractometer is used in processing of edible oils. This refractometer with cladding stripped silica fiber is used to measure refractive index with accuracy up to fourth decimal place for solutions of corn syrup mixed in water.

![Fig. 2.5 Schematic of an optical fiber refractometer](image)
b. Evanescent spectroscopic

The evanescent spectroscopic sensor design uses the evanescent field associated with the propagation of light in optical fibers. The evanescent fields can be used to transfer energy out of the core to absorbing species in the surrounding medium (evanescent absorption), to create fluorescence in the region outside the core (evanescent excitation) or to couple fluorescence from surrounding medium into the fiber core (evanescent collection). In the evanescent spectroscopic type design, shown in Fig. 2.6 the change in optical transmission properties is caused by optical absorbance of the analyte. These sensors require the analyte to be optically active (should show intrinsic fluorescence) in the wavelength range of the light in the optical fiber.

![Fig. 2.6 Schematic showing an evanescent spectroscopic sensor design](image)

Recent research in this area has therefore been focused mainly on pushing the wavelength range of this technique into the mid-infrared or the “chemical fingerprint” region of the electromagnetic spectrum. This design has found applications in in-situ gas diagnostics [28]. The sensor consists of an optical multi-mode
fused silica fiber with jacket and cladding removed and the bare fiber core in direct contact with the surrounding molecules. In this paper [28] results from first field measurements at the volcano site ‘Solfatara’ in Italy are reported that use such a sensor device for simultaneous detection of H₂S, CO₂ and H₂O directly in the gas stream of a volcano. Evanescent spectroscopic sensing design has also been applied in the area of biosensing for the detection of the Escherichia coli bacteria [29], the sensor described below uses a cladding striped multimode fiber as an intensity modulated sensor by evanescent absorption due to the existence of the bacteria. Fig. 2.7a & b shows a schematic drawing of the biosensor structure and set-up, respectively. The optical source is a 3-mW CW GaAlAs laser with graded-index multimode fiber pigtail, emitting at 840 nm. The output fiber is spliced with a bi-directional optical fiber coupler. Half of the emitted optical power propagates over the probe fiber (sensing element). The light modulated by the growing bacteria shown in the SEM micrograph Fig. 2.7 c, exits the fiber and is detected by the photodiode PD2. The other half of the optical power is detected by the photodiode PD1 from which an electrical reference signal. Both electrical signals are amplified and measured by a two channel calibrated optical-power meter. An AID board controlled by the LabVIEW software digitises both output signals from the optical power meter by means of its IEEE-488 interface. The AID board collects 800 points per
min of both sample and reference recording and storing the respective averages for a period of 24 hr per measurement cycle. The sensor device developed shows a sensitivity to as low as 10 bacteria particles, the developed device is also calibrated for sensitivity from 10 to 800 bacteria particles.

c. Coating based

Coating based sensors are the largest class of intrinsic fiber optic chemical sensors, in this design a small section of the optical fiber passive cladding is replaced by an active coating [30]. The analyte reacts with the coating to change the optical properties of the coating i.e. refractive index, absorbance, fluorescence etc which is then coupled to the core to change the transmission through the optical fiber. This fiber sensor design has found numerous applications from chemical sensing [20] to bio-sensing [12] and has also been applied to thermal and stress sensing [3]. A novel fiber optic hydrogen sensor which is constructed by depositing palladium over an exposed core region of a multimode fiber is reported [31]. The sensing mechanism is based on evanescent field interaction with the palladium coating. The transmission properties of palladium films are reported to change with hydrogen adsorption which leads to a change in the complex refractive index. Hydrogen diffusion into Pd leads to the formation of PdH which modifies the work function of Pd changing its electrical and optical properties. The reported sensor can detect hydrogen in the 0.2–0.6% range with corresponding response times of 30–20 s at room temperature. Sol-gel based microporous silica coatings which often serve as a matrix to the sensitive material have been extensively applied to optical
fiber coating based sensors for chemical and bio chemical sensing. An example of solgel based oxygen and pH sensor is shown in Fig. 2.8. The sensor reported [32] is fabricated by decladding a 10cm length of a 600 micron core polymer clad silica fiber. The fiber is then dip coated with a thin (approx 300nm) coating of sol-gel derived silica containing ruthenium [Ru(Ph2phen)_2] complex.

(a)

(b)
The fibers are then cured at 73°C for 24h to produce a tough, inert and highly adhesive coating on the fiber core as shown in Fig. 2.8 a. The experimental setup for the sensor test is shown in Fig. 2.8 b. The sensing element is connected with high intensity blue LED with 450nm peak emission. The fiber sensing element is mounted in a gas cell through which precise mixtures of nitrogen and oxygen is passed via mass flow controllers. The evanescent field of the guided light excites the entrapped ruthenium complex and a fraction of the fluorescence is captured by the fiber. The interaction of these excited ruthenium complexes with oxygen leads to fluorescence quenching and a decrease in the fluorescence intensity as shown in the sensor response Fig. 2.9. The pH sensor is fabricated in a similar way as the oxygen sensor except a different sensing die i.e. bromophenol blue is used. This dye shows increased absorption at higher pH. The reported sensor covers a pH range of 3-8. The sensor response for pH monitoring is shown in Fig. 2.10.
Fig. 2.8 (a) sol-gel coating based sensor design, (b) experimental setup for coating based optical fiber sensor for oxygen and pH sensing, A, collimating lens; B, launching lens; C, collecting lens; F, sensing fiber (in gas cell); D, short-wave pass filter; E, long-wave pass filter; L.I.A., lock-in amplifier [32].

Fig. 2.9 Sensor response for sol-gel coated sensor when exposed to 100% oxygen [32].
Core based sensors

Core based optical fiber sensors require use of special fibers made from porous glass. The core is sensitized by adding chemically sensitive reagents on the surfaces of the pores. The response time of these sensors is very long so this technique finds applications where very fast response is less important than sensitivity. There is very limited literature available for this type of sensor since there are very few research groups working in this area, also the fabrication of porous optical fiber can be a difficult task. In spite of the difficulties in this area pioneering work has been conducted by Macedo [33], Shahariari [34], and Zhou [35]. A reversible porous glass pH sensor has been reported with response in the range pH 4.0-7.0, also a reversible ammonia sensor with sensitivities in the lower ppm have been reported. Recently a novel sol-gel process for making porous
silica core fiber has been demonstrated [36] this fiber was then applied for humidity sensing.

The porous sol-gel fiber was prepared by pouring CoCl₂ doped sol-gel solution in a 0.7mm Tygon tube, after 2 days of gelation the gels were pushed out of the tubes and air dried to obtain the CoCl₂ doped sol-gel fiber. The fibers obtained by this technique had pore sizes ranging from sub-micrometer level to 2 microns, Fig. 2.11 shows an SEM micrograph of the fiber surface. Humidity sensor was constructed by cutting a 0.2cm length of the porous CoCl₂ doped solgel fiber and gluing this section between two commercial silica fibers with epoxy glue. This sensing element was then connected with a He-Ne laser (630nm) light source and a photodiode array photodetector.

The sensing element was placed in a climate chamber as shown in the Fig. 2.12 where controlled amount of humid and dry air was passed for humidity sensing. The sensor results shows sensitivity down to 2% relative humidity.
Fig. 2.11 SEM micrograph of CoCl$_2$ doped sol-gel fiber [36].
Fig. 2.12 Experimental set for porous CoCl$_2$ doped sol-gel fiber as a humidity sensor [36].

2.3 New Sensing Schemes

2.3.1 Microbent chemical sensor

Fiber bending losses have been compensated by using modulated light emitting diode and digital signal processing chips for a fiber optic fluorescent sensor [37]. This technique was demonstrated for fiber optic chemical sensing showing how micro-bend optical fiber can be used in chemical sensing [38]. In this type of sensor, permanent microbends are introduced in a plastic multimode step-index fiber 30cm in length and with a NA of 0.3, using corrugated plates and applying pressure. These corrugations have a pitch of 1mm and a total length of 60mm. This permanently bent optical fiber is used to detect chemicals having optical absorption at the operating wavelength. The corrugated
fiber section is submerged in a cell containing the chemical species and excited with a laser diode with operating wavelength of (670nm, 5mW) and used to detect Methylene Blue Dye in water. The intensity modulation due to the chemical absorption is measured separately in cladding modes and core modes using two photodetectors as shown in the Fig. 2.13.

2.3.2 SERS fiber sensor

The effect of surface-enhanced Raman scattering (SERS) has been exploited in single fiber sensor for chemical sensing [39]. The sensor consists of a single optical fiber with its end-face coated with Al₂O₃ nano-particles with silver coatings, which induce the SERS effect.

![Experimental setup for the microbent chemical sensor](image)

Fig. 2.13 Experimental setup for the microbent chemical sensor: L, diode laser(670 nm), C, cell containing MB in water, F, optical fiber, R, index-matching liquid, D₁, detector 1, D₂, detector 2 [38].

**SERS effect:** Raman scattering is a vibrational spectroscopic technique in which the monochromatic incident laser light is inelastically scattered from a sample and shifted in frequency by the energy of its characteristic molecular vibrations. In the case of conventional Raman Scattering no metal particles are present and the target analyte interacts directly with the incident electromagnetic field. In surface enhanced Raman
scattering effect the substrate is coated with metal colloids and the chemical to be examined is on this surface. This metal coating involves the creation of a surface plasmon on the substrate surface, which transfers energy through an electric field to the target molecules allowing otherwise inaccessible vibrational structure to be determined. The signal obtained is much enhanced in the case of SERS as compared to conventional Raman spectroscopy.

The SERS fiber sensor is made from an 8 cm long multimode fiber (600 microns diameter). The cladding and jacket is stripped (1 cm long) from one end and the fiber end is polished as shown in Fig. 2.14. This fiber is dip coated with alumina and then evaporation coated with silver to obtain a 1000 Å silver coating. This fiber section is excited with a He-Ne laser (wavelength 632.8 nm) with the silver coated section dipped in the sample solution. This single fiber carries both laser excitation and SERS signal, a Raman holographic Raman filter is used to separate the SERS signal. Using this scheme around 50 ppb of Cresyl fast violet (CFV) die has been detected in ground water.
2.3.3 SPR fiber sensor

Surface plasmon resonance (SPR) is the most popular method for optical biosensing. Surface plasmon resonance is a phenomenon which occurs when light is reflected off thin metal films. A fraction of the light energy incident at a sharply defined angle (SPR angle) can interact with the delocalized electrons in the metal film (plasmon) thus reducing the reflected light intensity. If binding of molecules occurs to the immobilized target the local refractive index changes, leading to a change in SPR angle, which can be monitored in real-time by detecting changes in the intensity of the reflected light.

The SPR fiber sensor setup is shown in Fig. 2.15. The sensor is made of an all silica/silicone fiber with 600microns diameter. The sensing element is prepared by removing the silicone cladding and coating this section with a 50nm silver film by thermal evaporation and covering this with thiol and actuator polymer (poly-3,3,3-trifluoropropyl-methylsiloxane and poly-3,3,3-trifluoropropyl-methylsiloxane 50% dimethylsiloxane copolymer. The polymers were deposited by dip coating. Vapors of chlorinated hydrocarbons and of aromatic compounds can be detected using the fluorosiloxane coatings [40]. The sensor developed shows a detection limit of 3000ppm for trichloroethylene and about 180ppm for xylene.
Fig. 2.15 Experimental setup for the SPR fiber sensor [40]
CHAPTER 3: OPTICAL FIBER SENSOR THEORY AND APPLICATION

3.1 Introduction

This chapter focuses on the structure of optical fibers, light propagation principles, and the modification of the optical fiber structure to form an intrinsic optical fiber sensor. The components of a general optical fiber sensor are discussed in detail. Also the developed optical fiber sensor, i.e. the modified cladding approach, is discussed in detail. This includes the evanescent mode, leaky mode and the partial leaky mode sensing mechanisms based on the relative refractive index of the modified cladding and the core.

3.2 Optical fiber waveguides

When light makes a transition from an optically dense medium (refractive index \( n \)) to an optically less dense medium (refractive index \( n' \)) the light rays are refracted away from the normal as shown in Fig. 3.1. According to Snell’s law the angle of refraction \( \theta_r \) is given by

\[
\theta_r = \arcsin \left( \frac{n' \sin \theta}{n} \right) \quad \text{where} \quad n' < n
\]  

(3.1)

The maximum value for the angle of refraction is 90°, in this case the ray grazes at the boundary surface, the corresponding angle in the dense medium is obtained from the eqn(3.1) above by substituting \( \theta_r = 90^\circ \).

\[
\theta_c = \arcsin \left( \frac{n'}{n} \right)
\]  

(3.2)
Fig. 3.1 Schematic showing ray traces form an optically dense medium to an optically less dense medium [41].

This angle is popularly known as the critical angle for total internal reflection, since any angle of incidence larger than the critical angle leads to total internal reflection i.e. no transition of radiation into the optically less dense medium takes place, instead the incident radiation is completely reflected into the optically dense medium at the interface. This phenomenon was first observed by J. Kepler in 1611 and is called total internal reflection.

An optical fiber is a cylindrical dielectric waveguide that transports energy at wavelengths in infrared and visible portions of the electromagnetic spectrum, using the total internal reflection phenomenon at the interface between two media with different refractive index as explained above. It has a central core in which light is guided, embedded in an outer cladding which has a slightly lower refractive index.
In order to form guided rays in the fiber the ray should be incident on the core such that upon refraction into the core it makes an angle smaller than $\theta_c'$ with the fiber axis shown in Fig. 3.2. In order to couple light into the optical fiber the light should be incident within the acceptance cone described by the acceptance angle of the fiber, undergo total internal reflection and form guided modes, see Fig. 3.2. Light incident outside this cone lose part of their power to the cladding at each reflection and are not guided (leaky modes). The acceptance angle $\theta_a$ at the air-fiber tip boundary can be calculated by applying snells law at the air-fiber tip interface and at the fiber core-cladding interface given by eq. 3.3 below

$$\theta_a = \sin^{-1} \text{NA} \quad (3.3)$$

Where

$$\text{NA} = \sqrt{n_1^2 - n_2^2} \quad (3.4)$$

Here NA is known as the numerical aperture of the optical fiber it describes the light gathering capacity of the optical fiber and $n_1$ and $n_2$ are refractive index of core and cladding respectively.

**Guided Modes**

If a path of a ray is entirely confined in the core by total internal reflection, this ray is referred to as a guided or bound ray, as shown in Fig. 3.2 & Fig. 3.3a. These rays are categorized by a value of $\theta_z$, see Fig. 3.3a according to the condition given below

**Bound or guided rays:** $0 \leq \theta_z < 90 - \theta_c$. 

The power of the bound ray is contained completely in the core and can propagate indefinitely without loss of power.

Fig. 3.2 Schematic showing optical fiber structure, light intensity distribution and geometric ray dynamics within the fiber.

In the case of guided rays, the electromagnetic fields do not abruptly reduce to zero at the interface between core and cladding. The electromagnetic field decays...
exponentially with distance starting from the interface extending into the cladding this extended field is called **evanescent field**, shown in Fig. 3.2. The penetration depth of the evanescent field in the cladding is given by the eq. 3.5 [43]

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

(3.5)

Where \(d_p\) penetration depth of evanescent field

- \(\lambda\) wavelength of light
- \(\theta\) angle of incidence
- \(n_1\) refractive index of core
- \(n_2\) refractive index of cladding

Optical fiber sensors extensively make use of the evanescent field – analyte interaction as their sensing principle, these sensors are known as evanescent field sensors. The evanescent field in the cladding region can directly interact with the analyte producing absorbance or fluorescence that can be coupled into the fiber core producing intensity modulation.

**Refracting or leaky modes**

If the ray is only partially reflected at each reflection shown in Fig. 3.2 & Fig. 3.3b, these modes are referred to as leaky or refracting modes. The rays may be characterized by the value of \(\theta_z\) according to the condition given below.

**Refracting or leaky rays:** \(90 - \theta_c \leq \theta_z \leq \pi/2\).

The refracting ray loses a fraction of its power in every reflection and attenuates as it propagates.
3.3 Optical Fiber Sensor

There are four basic types of light property modulation used in optical fiber sensors: intensity, phase, wavelength, and polarization. These light properties can be modulated by changing the boundary conditions through different types of physical perturbations which include chemical, biological, mechanical, electrical, magnetic, thermal and radiation. The general structure of an optical fiber sensor system is shown in the Fig. 3.4. It consists of an optical source (Laser, LED, Laser diode etc), optical fiber, sensing or modulator element (which transduces the measurand to an optical signal), an optical detector (photodiode) and processing electronics (oscilloscope, optical spectrum analyzer etc).

![Fig. 3.4 Schematic showing the general system set-up for an optical fiber sensor [44].](image)

Light source:

The selection of the light source depends on the wavelength region in which the transducer shows the maximum response. For example, polyaniline transducer based sensors for ammonia show maximum absorbance change at 632.8nm, so when polyaniline is used as a transducer in optical fiber sensors for ammonia sensing a He-Ne laser (632.8nm) source would be ideal for maximum sensor response. LEDs and
other broad band sources may be used with multimode fibers, but single mode fibers may require coherent LD sources.

**Optical fiber:**

For intensity modulation based sensors multimode optical fibers are generally used, single mode fibers are used in interferometric fiber sensors where phase changes are measured. Low loss silica core fibers are preferred where fiber lengths used is large where fiber losses become considerable.

**Transducer:**

The choice of the modulator is based on the kind of sensing desired form the optical fiber sensor. In many cases the optical fiber itself plays an active role as a transducer e.g. microbend sensor. In cases where chemical sensing is desired the fiber is either modified to incorporate the transducer or simply connected to the transducer. The choice of the transducer in the case of chemical sensing is based on the optical property change in the material due to the chemical presence.

**Detector:**

Detection is based on the type of light modulation technique used. For phase modulation, interferometric detection is used, while for polarization modulation polarization analyzer is used. However, in wavelength modulation the spectrum analyzer is used. Incase of intensity modulation, which is common for most chemical sensors, the detectors used are the conventional photodiodes depending on the wavelength of the light source and the wavelength region of the sensor response. Sensor setups where the response is very weak make use of high sensitivity APD (avalange photodiodes) which have very high gains.
Electronic processing:

The electronic processing unit of the sensor system may involve any power meter, oscilloscope, optical spectrum analyzer or computer to which the sensor response is feed from the detector for further analyses and processing.

3.4 Optical Fibers for Chemical Sensing

There are several potential advantages of using optical fibers as sensors in chemical sensing these include suitability for remote in-situ measurements, freedom from electromagnetic interference and potential of distributed sensing. Optical fiber chemical sensors involve probing matter by photons. Various light parameters are associated with this photon flux and may give useful information about the material being probed.

In the current work we concentrate on intensity modulation in multi-mode fibers using a chemical transducer to convert analyte presence to optical information and lead to sensing using optical fibers. The optical parameter that is modulated by the chemical is the material complex refractive index. The complex refractive index modulation in the transducer material is achieved by changes in materials absorbance and dielectric properties (conductivity) of the transducer material due to the presence of analyte. The origin of the changes in absorbance and conductivity lie in the material property change in the transducer such as material crystallinity. The detail of the design for the optical fiber sensor using an on-fiber transducer material for chemical sensing is given in the next section.
3.5 Sensor Design

The optical fiber sensor developed in this work is based on the modified cladding or coating design. The passive cladding of the optical fiber is removed from a small section and is replaced by a chemo-chromatic material as shown in Fig. 3.5. When the chemochromic material interacts with analyte the material refractive index changes. The refractive index is a complex quantity given by

\[ n_{\text{complex}} = n_{\text{real}} + ik \]

where \( n_{\text{complex}} \) is the complex refractive index of the material

\( n_{\text{real}} \) Real part of the refractive index

\( k \) complex part related to the absorbance of the material.

Any change in the real refractive index or the absorbance of the material due to the presence of the analyte, changes the transmission properties of the optical fiber. There can be three different modes of operation of the sensor depending upon the refractive index of the chemo chromic material \( (n_{\text{mc}}) \) relative to the refractive index of the core \( (n_1) \) and the refractive index of the original cladding \( (n_2) \).
**Case 1: Evanescent mode \( \{n(\text{cladding}) = n(\text{modified cladding}) < n(\text{core})\} \)**

In this case since the refractive index of the modified cladding is equal to that of the original cladding the wave-guiding conditions do not change in the modified region and the light has the same Gaussian intensity profile throughout the fiber core and evanescent field in the cladding. Any change in the absorbance of the modified cladding material will result in evanescent absorption and the intensity of the light will change, as shown in Fig. 3.6.

![Fig. 3.6 Schematic for case 1 where \( \{n(\text{cladding}) = n(\text{modified cladding}) < n(\text{core})\} \)](image)

**Case 2: leaky mode \( \{n(\text{modified cladding}) > n(\text{core}) > n(\text{cladding})\} \).**

In this case the refractive index of the modified cladding is greater than the refractive index of the core as well as that of the original cladding, Fig. 3.7. But the medium surrounding the modified cladding is air that has a refractive index much lower than that of the modified cladding. The boundary between the air and the modified cladding can support total internal reflection and some light is reflected back into the core leading to transmission of light through the modified region. Any change in the refractive index of the modified cladding due to the analyte can change
the condition of total internal reflection between the modified cladding and air and can result in an intensity change.

Fig. 3.7 Schematic for case 2 where \(n(\text{modified cladding}) > n(\text{core}) > n(\text{cladding})\)

**Case 3: Partial leaky mode \(n(\text{cladding}) < n(\text{modified cladding}) < n(\text{core})\).**

In this case the sensor operates in the partial leaky mode Fig. 3.8 i.e. the critical angle in the modified region is larger than the angle for the fiber, so some higher order modes will leak through the modified cladding and the lower order modes will continue to propagate as guided modes. Any change in the real part or the complex part (absorbance) of the refractive index can lead to a change in the transmitted intensity.

Fig. 3.8 Schematic for case 3 where \(n(\text{cladding}) < n(\text{modified cladding}) < n(\text{core})\)
3.6 Conclusion

It is apparent from the structure and the light guiding properties of the optical fiber that the structure of the optical fiber can be modified for chemical sensor applications. After taking a close look at the light material interaction in the fiber it can be concluded that light intensity modulation can be brought about by an interaction of the chemical species with the evanescent field or refracting rays in an optical fiber, in the modified cladding region. The modified cladding approach can provide with an excellent sensor design, to sense toxic chemical species using an appropriate transducer. The following chapter 4 discusses the transducer material using polypyrrole as the modified cladding. Details on the polymer structure, properties and its ability to sense DMMP is presented.
CHAPTER 4: PROCESSING AND CHARACTERIZATION OF THE CHEMO-CHROMIC MATERIAL

4.1 Introduction

Organic conducting polymers (OCPs) have a unique ability to show both the mechanical properties of a polymer and electrical properties of a conductor which has attracted interest in potential technological applications. OCPs such as polypyrrole, polyaniline, polythiophene, polyindoles and polyacetylenes show a reversible change in their resistance when exposed to certain vapors. These materials are easy to prepare, show excellent ambient stability and show a very rapid and reversible adsorption/desorption kinetics. Therefore they have attracted much attention in the area of gas sensing. The research in gas sensing employing OCPs as transducers has progressed in various ways which include, Langmuir-Blodgett thin films[45, 46], Multi-electrode sensor array [47], as coatings for Quartz Crystal Microbalance sensors [48] and as modified cladding’s in optical fiber sensors [5][49]. Polyacetylene (CH)ₓ was the first OCP characterized in 1977, but lack of physiochemical stability in polyacetylene lead to the development of heterocyclic OCPs.

In heterocyclic OCPs the \( \pi \)-system is retained for conductance but a heteroatom is included in the structure to complete a five membered ring structure. Polypyrrole is one of the most stable of the heterocyclic OCPs under ambient conditions [50]. The gas sensing ability in terms of sensitivity and selectivity of polypyrrole can be tailored by adding different dopant anions.
This chapter begins with an introduction section on the structure, and the state of the art of the DMMP sensing technology using polypyrrole films as transducer element. Polypyrrole thin films are prepared using both the in-situ and monomer vapor phase deposition techniques. Polymer identification characterization is conducted using Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. ESEM characterization is performed for polymer morphology study. Electrical property measurement of the polypyrrole is performed using four probe technique. Refractive index measurement is conducted using Ellipsometry for the real part. The complex part of refractive index i.e. extinction coefficient is calculated using the thin film transmission experiment. In-situ exposure of DMMP to polypyrrole films is conducted to measure the complex refractive index change, using ellipsometry and thin film transmission experiments. Conductivity change in polypyrrole films upon DMMP exposure is measured using the four-probe setup.

4.2 Polypyrrole

The base unit of polypyrrole is pyrrole, the structure of which is a five membered heteroaromatic ring containing a nitrogen atom as shown in Fig. 4.1 a. Polypyrrole is synthesized from the pyrrole monomer by mild oxidation, using chemical or electrochemical technique. After the oxidation of the monomer a black solid polymer is precipitated from the solution, the polypyrrole structure in its neutral and oxidized form is shown in Fig. 4.1 b
4.3 Polypyrrole Sensors

A large number of gas sensors make the use of conducting polymers as their transducer element since they have great design flexibility and are very stable at ambient temperature and pressure. Conductivity and work function of conducting polymers are the two main properties that are used in chemo-electric, chemomechanic or chemo-chromic transduction. It is reported that the conducting polymer polypyrrole shows a

![Fig 4.1 (a) Pyrrole monomer base unit, (b) Polypyrrole in neutral and oxidized form.](image)

change in conductivity [7] and work function [51] when exposed to DMMP. The following two sections describe how conducting polymers can be used in constructing a sensor device that uses conductivity and work function modulation to sense DMMP and other gases.

4.3.1 Conductivity modulation

A chemiresistor device shown in Fig. 4.2 is an example of a conducting polymer gas sensor making the use of conductivity modulation as a sensing
mechanism. A chemiresistor consists of a pair of electrodes forming contacts to the CP, deposited on an insulating substrate. When constant current is applied, the resulting potential difference at the electrodes becomes the signal. Conductivity modulation in a material can be brought about by changing the number of charge carriers or by changing the bulk mobility eq. 4.1

$$\sigma = en\mu$$  \hspace{1cm} (4.1)

where \(\sigma\) is conductivity.

- \(e\) charge of an electron
- \(n\) concentration of charge carrier.
- \(\mu\) mobility of charge carrier.

When an electronically active gaseous species interacts with the conducting polymer it can act as an electron donor or electron acceptor. If the conducting polymer is p-type (polypyrrole) then it donates an electron to the gas and its hole conductivity increases. If an inert gas interacts with the CP it can bring about
conformational changes in the polymer backbone i.e. the CP goes form a coiled up chain to an expanded chain conformation which results in a change in the charge transport pathways and hence the mobility of the charge carriers. The main disadvantage of this type of sensor device is that the response from the bulk of the CP has relatively long time constants some times in minutes. The long time constants are mainly due to the slow penetration of gases into the CP. Collins and Buckley [7] have demonstrated a conductivity change in thin films of polypyrrole coated onto poly(ethylene terephthalate) PET fabrics (a device similar to a chemiresistor) shown in Fig. 4.3 when exposed to 28ppm of DMMP.

Fig. 4.3 Resistance change in polypyrrole coated onto PET fabrics when exposed to 28ppm DMMP [7].

4.3.2 Workfunction modulation

A Field-effect transistors (FET) shown in Fig. 4.4 makes use of work-function modulation as a sensing mechanism. Work function is defined as the energy difference between the Fermi energy level (highest occupied level in the band-gap at a given temperature) and the vacuum level. In a chemically sensitive FET (CHEMFETs) the CP whose work function is modulated, forming an interface with
the thin solid dielectric material usually silicon nitride/ silicon dioxide. It is at this interface that the gas molecule adsorbs and forms an electrical dipole modulating the work function. The main problem with this device is the quality of contact between the CP and the dielectric thin films. Karin [51] has shown a change in work function of metallophthalocyanines (MPcTS) doped polypyrrole by kelvin-probe method Fig. 4.5 when exposed to 44ppm of DMMP.

From the sections (4.3.1) and (4.3.2) we see that, polypyrrole can act as a chemo-chromic transducer material to sense DMMP in a fiber optic chemical sensor based on the modified cladding design, since a change in the conductivity or work-
function will change the complex permittivity which leads to a change in the complex refractive index through the following equations.

\[
    n^* = \left[ \frac{1}{(\varepsilon^* \varepsilon_0)} \right]^{1/2} \tag{4.2}
\]

\[
    \varepsilon^* = \varepsilon - i\sigma/\omega \tag{4.3}
\]

where,

- \( n^* \) is the complex refractive index
- \( \varepsilon^* \) is complex dielectric permittivity
- \( \sigma \) is the conductivity.

Fig. 4.5 Workfunction change in polypyrrole doped with various anions in the presence of NO₂, PER, DMMP in ambient air, measured with Kelvin probe method [51].
4.4 Polypyrrole Synthesis.

Polypyrrole samples were synthesized using the in-situ chemical deposition process and the monomer vapor phase deposition process. Both techniques utilize the oxidation of the pyrrole monomer. Samples were prepared on glass (SiO₂) substrates for SEM, thin film transmission and conductivity characterization and on p-type silicon wafers for ellipsometry characterization.

4.4.1 In-situ deposition

In-situ deposition of polypyrrole was carried out by mixing the oxidant solution with the monomer solution while the substrates are dipped in the solution and stirred with a magnetic stirrer. The oxidant solution is a mixture of 100ml deionized water, 3.5g of FeCl₃-6H₂O (oxidant) and 1M dopant acid (HCl, NDSA or ASQA). The monomer solution which consists of a 100ml deionized water and 0.6ml of pyrrole monomer is then added to the oxidant solution with the substrates dipped inside. After a few minutes the polymerization takes place and the solution turns from orange to black. Deposition takes place as the polymerization continues.

4.4.2 Chemical vapor deposition

This method uses one of the reagents i.e. either the oxidant or the monomer in vapor phase. In this work the substrate is coated with the oxidizer FeCl₃-6H₂O by spin coating technique. The SCS/G3P-12 spin coat system (Speciality coating
systems) was used for spin coating, the oxidizer was dissolved in acetone and dropped on the substrate revolving at 500 rpm. The oxidizer coated section of the substrate is exposed to pyrrole monomer vapor solution. The monomer vapor polymerizes around the substrate in contact with the oxidizer, a very thin and uniform layer of polypyrrole film is obtained on the substrate.

In both the deposition techniques i.e. in-situ or monomer vapor phase deposition, the polymerization mechanism remains the same as shown in Fig. 4.6. The pyrrole ring is oxidized by the oxidizer (ferric chloride) to form a radical cation, which reacts with another radical cation to form a dimer by elimination of two protons. The dimer that is formed is more susceptible for oxidation than the monomer and further reacts to give higher order oligomers. These oligomers grow to precipitate in the solution and on the substrate to eventually form polypyrrole films. Typical chains produced by this technique have 100-1000 monomer units [50]. The termination of the polymerization reaction may occur by water attacking the radical cation to form hydroxyl group at 4 or 5 position, which can be further oxidized to form a carbonyl group. Since polypyrrole has a lower oxidation potential as compared to its monomer, the polymer chain contains a number of positive charges spread over the chain of the structure. The positive charge spread is over 3-4 monomer units and this charge is balanced by the counterion incorporated during the oxidation process.
4.5 Polypyrrole Characterization

Chemical finger print characterization of the polymer was done by Infrared (IR) and Raman spectroscopy. Infrared and Raman spectroscopy being complementary to each other can provide with a detailed chemical identification of polypyrrole.

4.5.1 Infrared spectroscopy

Infrared spectroscopy is an important technique in organic chemistry. The infrared spectrophotometer provides a record of the infrared absorbance or transmittance of a sample as a function of wave number. The frequencies at which
absorption occurs may indicate the type of functional groups present in the polymer. There are several research groups [52-54] that have made assignments to vibrational modes of polypyrrole. FTIR for both in-situ as well as monomer vapor phase deposition was performed using the Digilab UMA-600 Micro-FTIR. The infrared spectra of polypyrrole film prepared by in-situ deposition and monomer vapor deposition using the FeCl$_3$ oxidant in the region 2000 to 700 cm$^{-1}$ is shown in Fig. 4.7 & Fig. 4.8 respectively. The band occurring at 1540 cm$^{-1}$ corresponds to the C-C stretching vibration in polypyrrole ring. The band occurring at 1459 cm$^{-1}$ for insitu deposition corresponds to the C-N stretching vibration in the ring. The broad band from 1400 to 1250 cm$^{-1}$ for insitu deposition is attributed to C-H or C-N in-plane deformation modes. The polypyrrole ring breathing vibration is found in the region between 1250 to 1100 cm$^{-1}$, with a maximum situated at 1116 cm$^{-1}$ for insitu deposition and 1220 cm$^{-1}$ for vapor deposition. The other bands include C-H and N-H in-plane deformation vibration at 1080 cm$^{-1}$ and the C-C out of plane ring deformation vibration at 952 cm$^{-1}$ the same bands occur at 1056 cm$^{-1}$ and 945 cm$^{-1}$ for vapor deposition. The C-H out of plane vibration arises at 915 cm$^{-1}$ for insitu deposition and 877cm$^{-1}$ for vapor deposition. The peak at 820 cm$^{-1}$ represents the C-H out of plane ring deformation for insitu and 823cm$^{-1}$ for vapor deposition.
Fig. 4.7 FTIR spectra of insitu deposited polypyrrole for 5, 10 and 30 min insitu deposition.

Fig. 4.8 FTIR spectra for monomer vapor deposited polypyrrole for 1, 2.5 and 5 min vapor deposition
4.5.2 Raman spectroscopy

Raman spectroscopy was performed on in-situ and vapor phase deposited polypyrrole films on silicon substrates using the Raman Micro Spectrometer (Renishaw 1000) employing a 633nm He-Ne laser using 25% of 50mW total power. Raman spectroscopy is one of the important techniques to obtain structural information of polypyrrole.

Fig. 4.9 shows the schematic of a Raman micro spectrometer. There have been many researchers who have studied Raman spectra of polypyrrole [52, 55-56]. Raman Spectroscopy is based on the Raman effect, which is the inelastic scattering of photons by molecules. The effect was discovered by the Indian physicist, C. V. Raman in 1928. The Raman effect arises when the incident light excites molecules in the sample which subsequently scatter the light. While most of this scattered light is at the same wavelength as the incident light, some is scattered at a different wavelength. This in-elastically scattered light is called Raman scatter. It results from the molecule changing its molecular motions. The energy difference between the incident light (Ei) and the Raman scattered light (Es) is equal to the energy involved in changing the molecule's vibrational state (i.e. getting the molecule to vibrate, Ev). This energy difference is called the Raman shift.

\[ Ev = Ei – Es \]  \hspace{1cm} (4.4)

Several different Raman shifted signals will often be observed; each being associated with different vibrational or rotational motions of molecules in the sample. The
particular molecule and its environment will determine what Raman signals will be observed. A plot of Raman intensity vs. Raman shift is a Raman spectrum.

Figs. 4.10 and Fig. 4.11 show the Raman spectrum of insitu and monomer vapor phase deposited polypyrrole samples respectively. The sharp peak occurring at 1593 cm\(^{-1}\) may be attributed to C-C and C=C ring stretching and N-H in plane bending vibration. The low intensity peak at 1502 cm\(^{-1}\) may be attributed to C=C and C-N ring stretching and C-H in plane bending vibration. The broad peak at 1383 cm\(^{-1}\) may be due to the C-H and N-H in-plane bending vibration. The peak at 1249 cm\(^{-1}\) may be attributed to the C-C inter-ring stretch and C-H, N-H in plane bending vibration. The peak at 1089 cm\(^{-1}\) may be attributed to C-H and N-H out-of-plane bending vibration and the peak at 1064 cm\(^{-1}\) is attributed to C-C ring stretching and C-H in-plane bending vibration. The peaks at 933 cm\(^{-1}\) and 967 cm\(^{-1}\) are attributed to C=C ring stretching and C-H and N-H ring in-plane bending vibration.

Fig. 4.9 Schematic of a micro-raman spectrometer
Fig. 4.10 Raman spectra of polypyrrole films on silicon substrate for 5, 10 and 30 min in-situ deposition time.

Fig. 4.11 Raman spectra of polypyrrole films on silicon substrate for 0.5, 1, 2.5 and 5 min in-situ deposition time.
4.6 Polypyrrole Application for Sensing DMMP.

4.6.1 Conductivity measurements

Conductivity measurements on the polypyrrole films were conducted using the four probe setup shown in Fig. 4.12. The four probe technique is used for direct measurement of bulk material resistivity, eq.4.5 & 4.6 and sheet resistance of thin films eq. 4.7. A known current is forced through the outer probes, and the voltage developed is measured across the inner probes. The resistivity and sheet resistance can then be calculated using the eq. 4.7 below.

\[ \rho = \frac{2\pi s V}{I} \text{ for } t \gg s. \]  
\[ \rho = \frac{\pi t}{\ln 2} \frac{V}{I} \text{ for } s \gg t. \]

For thin films, sheet resistance

\[ R_s = \frac{\rho}{t} = \frac{\pi}{\ln 2} \frac{V}{I} = 4.53 \frac{V}{I} \text{ for } s \gg t. \]

Where \( \rho \), resistivity of the bulk material

\( R_s \), sheet resistance of thin film

\( t \), film thickness

\( s \), probe spacing

\( V \), voltage drop

\( I \), applied current
Conductivity measurements were performed on polypyrrole thin films doped with HCL, NDSA and ASQA. The I/V characteristics show a linear increase in voltage drop across the inner probes as the current on the outer probes is increased from 0 to 15 mA. The I/V characteristics show highest conductivity for the ASQA and then NDSA doped polypyrrole, attributable to the primary doping in the polymer due to addition of the dopant in the polypyrrole structure.

Fig. 4.13 I/V characteristics of polypyrrole films deposited on glass substrates.
**DMMP sensing property**

The gas sensing property of NDSA doped polypyrrole towards DMMP, was investigated by in-situ DMMP exposure to films under the four probe, a constant current of 1mA was maintained across the outer probes and the change in voltage on the inner probes was measured by exposing the thin films to DMMP vapor. The sheet resistance change in the film was measured using the eq. 4.7. The change in the sheet resistance of the polypyrrole film can be seen in Fig. 4.14.

![Resistance change in NDSA doped Polypyrrole exposed to DMMP](image)

Fig. 4.14 Resistance decrease in NDSA doped polypyrrole films when exposed to DMMP vapor.

**DMMP-Polypyrrole interaction**

When an electronically active gaseous species interacts with the conducting polymer it can act as an electron donor or electron acceptor. If the conducting polymer is p-type (polypyrrole) then it donates an electron to the gas and its hole
conductivity increases, this phenomenon is termed as primary doping (Fig. 4.1b) [50, 57]. If an electronically inert vapor (does not remove or add charge to the polymer backbone) e.g. DMMP, interacts with a primarily doped CP it can bring about conformational changes in the polymer backbone i.e. the CP goes form a coiled up chain to an expanded chain conformation which results in a change in the charge transport pathways and hence the mobility of the charge carriers. Fig. 4.15 shows the process of secondary doping [58]. For a charged polymer chain, the electrostatic repulsion between similarly charged units of the chain will occur, this repulsion becomes greater when the distance between a charged unit on the chain and its counterion is increased i.e. when the repulsion forces are greater than the attraction force. If for instance the counterion associated with a positively charged were remote infinity, the resulting larger cumulative electrostatic repulsion between the positive charges would tend to produce linearity of chains. Thus any effect of increasing the distance between the positive and negative charges such as solvation of the cations and/or anions will tend to expand the compact coil conformation of the polymer chain. This conformation change increases the crystallinity of the polymer which further increases the mobility of the charge carriers increasing the conductivity of the bulk polymer, which in turn changes the refractive index.
Ellipsometry measurements were carried out using the Woolham M 2000 U ellipsometer fabricated by the J. A. Woolham Co. The principle of ellipsometry used to characterize the optical properties of thin films has been reviewed by many authors [59-60]. Ellipsometry is a very sensitive measurement technique that uses polarized light to characterize thin films. Ellipsometry involves the measurement of the change in the state of polarization of the incident light beam after reflection from the surface of interest. The probe beam is of known polarization state i.e linearly polarized is converted to elliptically polarized reflected beam. Fig. 4.16 shows the schematic geometry for the sample measurement. These polarization state changes are described by the ellipsometric angles $\Psi$ and $\Delta$. These values are related to the Fresnel reflection coefficients $R_p$ and $R_s$ for p and s polarized light respectively eq. 4.8.

$$ P = \frac{R_p}{R_s} = \tan(\Psi)e^{i\Delta} \tag{4.8} $$

Because ellipsometry measures the ratio of two values it can be highly accurate and very reproducible. The Levenberg-Marquardt multivariate regression algorithm
Fig. 4.16 Schematic showing linearly polarized light reflection from the surface of a sample to change to elliptically polarized light.

was employed for the fitting process. Thin films were deposited on p-type silicon substrates using 5min, 10min and 30min in-situ deposition. The spectra of ellipsometric angles $\Psi$ and $\Delta$ were made in a spectral range of 245nm to 1000nm, using a broad band Xenon arc lamp.

Fig 4.17 shows the $\Psi$ and $\Delta$ v/s wavelength spectra for the experimental and the model fit for the 5 min in-situ deposited films. The refractive index values recorded for the 5min, 10min and 30min deposition sample were 1.67, 1.88 and 1.97 respectively. These values of refractive index for NDSA doped polypyrrole films indicate that when applied as modified cladding it will lead to a leaky mode operation of the fiber sensor as the refractive index of the polypyrrole modified cladding is greater than the core and cladding refractive index. In-situ experiments to record the
change in refractive index of NDSA – doped polypyrrole films upon DMMP exposure were conducted. The DMMP vapor was puffed on the 5min in-situ deposited film surface using a syringe, the refractive index values were measured before and after exposure. The results reveal an increase in refractive index from 1.677 before exposure to 1.7238 after DMMP exposure, as shown in Table 4.1. This increase is attributed to the conductivity increase in polypyrrole films due to DMMP adsorption. It is believed that DMMP interacts with the polypyrrole to increase the number and mobility of the hole charge carriers in the polymer back bone [7, 51].

Fig (4.17) Ψ and Δ v/s wavelength spectra for the experimental and the model fit for the 5 min in-situ deposited films using ellipsometry.

4.6.3 Thin film transmission

Thin film transmission experiment was designed to calculate the absorbance change in NDSA doped polypyrrole films upon DMMP exposure. The experimental setup shown in Fig. 4.18 uses a He-Ne laser (wavelength 633nm). A neutral density filter is used in the set-up to reduce the intensity of light
Table 4.1: Refractive index values before and after DMMP exposure

<table>
<thead>
<tr>
<th>Deposition</th>
<th>Refractive index (before DMMP exposure)</th>
<th>Refractive index (after DMMP Exposure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insitu deposition</td>
<td>1.6777</td>
<td>1.7238</td>
</tr>
<tr>
<td></td>
<td>1.6455</td>
<td>1.8926</td>
</tr>
<tr>
<td>Vapor phase deposition</td>
<td>1.8675</td>
<td>2.0172</td>
</tr>
<tr>
<td></td>
<td>2.0767</td>
<td>2.1590</td>
</tr>
</tbody>
</table>

Fig. 4.18 Schematic of the experimental setup for measuring the absorbance of polypyrrole thinfilms.

seen by the detector. Table 4.2. shows the transmitted light intensity before and after the film insertion in the light path is recorded to calculate the absorbance of the film using the eq. 4.9. The thin film thickness was measured using the cross section SEM image of the thin film as shown Fig. 4.19.

\[ A = \log(I_o/I) = (az)/2.303 \]  
\[ k = \alpha(\lambda/2\pi) = (2.303A\lambda)/(2\pi z) \]
Where A specimen absorbance

k extension coefficient

$I_0$ is direct intensity without the sample

I is the intensity with sample in its path

\( \alpha \) is the absorption coefficient

z sample thickness

\( \lambda \) wavelength of the light source used

Table 4.2: Transmission through polypyrrole thin films

<table>
<thead>
<tr>
<th>Material</th>
<th>Direct power</th>
<th>Glass slide</th>
<th>Sample</th>
<th>Absorbed power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ppy-FeCl₃</td>
<td>1.91</td>
<td>1.76</td>
<td>0.48</td>
<td>1.28</td>
</tr>
<tr>
<td>Ppy-HCl</td>
<td>1.61</td>
<td>1.48</td>
<td>0.36</td>
<td>1.12</td>
</tr>
<tr>
<td>Ppy-NDSA</td>
<td>1.57</td>
<td>1.43</td>
<td>0.35</td>
<td>1.08</td>
</tr>
<tr>
<td>Ppy-ASQA</td>
<td>1.60</td>
<td>1.45</td>
<td>0.73</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 4.3: transmission change in NDSA doped polypyrrole films upon DMMP exposure

<table>
<thead>
<tr>
<th>Ppy-NDSA</th>
<th>Initial power</th>
<th>Glass slide</th>
<th>Film</th>
<th>DMMP exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1.600</td>
<td>1.520</td>
<td>0.373</td>
<td>0.356</td>
</tr>
<tr>
<td>Sample 2</td>
<td>2.22</td>
<td>2.01</td>
<td>0.430</td>
<td>0.421</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1.549</td>
<td>1.441</td>
<td>0.348</td>
<td>0.344</td>
</tr>
</tbody>
</table>
The calculated extinction coefficient for the thin film using the eqn (4.10) above is 0.06768. The film was then exposed to DMMP and the transmission through the film was recorded in real time as shown in the Fig. 4.20 and Table 4.3. As seen from the result the transmission through the film has decreased by 4.6 %. The extinction coefficient for the film after the DMMP exposure is 0.07017. This increase in the absorbance is attributed to the change in the number of charge carriers in the polymer back bone due to DMMP adsorption.

4.7 ESEM Characterization

ESEM characterization of both in-situ and vapor phase deposition was conducted using the FEI/Phillips XL30 FESEM. Fig. 4.21 show a low resolution micrograph of the film microstructure of polypyrrole film deposited insitu for 30 min on glass substrate. It can be seen from the micrograph that the film structure is not
uniform and has folds of the order of about a micron in the microstructure as shown in Fig. 4.22. These folds may be attributed to the penetration of the solution in the groves between the film and the glass substrate during solution polymerization.

Fig. 4.20 Polypyrrole thin film transmission change before and after DMMP exposure

The SEM microstructure of the monomer vapor phase thin film samples are shown in Fig. 4.23. The low magnification SEM micrographs show a dendrite growth of polymer, when pyrrole monomer vapor comes in contact with the substrate coated with the oxidizer ferric chloride. Fig. 4.24 shows a high magnification image of the dendrite structure in the thin film. This type of microstructure may have originated due to concentration fluctuation in the oxidizer through the film or due to other impurities on the surface of the substrate, which may serve as a nucleation site for the formation of such dendrites.
Fig. 4.21 SEM micrograph of a 30 min insitu deposited polypyrrole film on glass substrate

Fig. 4.22 High magnification SEM micrograph of a 30 min insitu deposited polypyrrole film on glass substrate
Fig. 4.23 SEM micrograph of a 5min vapor deposited polypyrrole film on glass substrate

Fig. 4.24 High magnification SEM micrograph of a 5min vapor deposited polypyrrole film on glass substrate
4.8 Conclusion

This chapter establishes that polypyrrole thin films have been successfully used in thin film sensors i.e. as a chemiresistors and chemochromic transducer element for detection of DMMP. This gives us a base to select and apply polypyrrole to on-fiber sensor devices to detect DMMP.

1) Polypyrrole is successfully synthesized in the form of thin films on glass and silicon substrates and characterized using Microraman and FTIR characterization techniques.

2) The DMMP sensing property of these thin films are established using the Four-probe conductivity measurement setup for conductivity modulation in thin films followed by DMMP exposure, ellipsometry and thin film transmission experiments for real and complex refractive index modulation followed by DMMP exposure. It is clear from these experiments that polypyrrole thin films show an increase in conductivity and an increase in refractive index when exposed to DMMP vapor. These experiments establish the fact that polypyrrole can be used as an active material transducer in optical and electronic sensor devices to sense DMMP vapor.

3) The surface morphology study indicates a uniform film surface in the case of in-situ deposition and a dendrite growth in case of monomer vapor phase deposited polymer.
The following chapter 5 is based on the application of the polypyrrole thin film developed in this chapter as a modified cladding to optical fibers to develop optical fiber sensor device.
CHAPTER 5: SENSOR DEVELOPMENT

5.1 Introduction

This chapter is focused on the development, characterization and optimization of the fiber optic chemical sensor presented in this work. The foundation of the developed sensor is based on the change of optical power or optical intensity modulation induced within modified multimode optical fibers [61]. The sensor design is based on using the modified cladding technique, i.e. the DMMP sensitive material, polypyrrole is coated on a small section of the fiber, replacing the original cladding. The experimental results show a positive response of polypyrrole coated optical fiber to DMMP vapor. The sensor developed in its early stage has shown a very limited sensitivity, of only 2.1 % intensity change, at room temperature, when exposed to vapor pressure of approximately 134 ppm of DMMP [62]. To enhance the sensor response and sensitivity several techniques were under investigation. First, the polymer material was doped with three different types of dopants i.e. 1, 5 Naphthalene di sulphonic acid (NDSA), Anthraquinone 2 sulphonic acid (ASQA) and Hydrochloric acid (HCL). Second, two coating techniques i.e. in-situ deposition and monomer vapor phase deposition have been investigated, to find which provides the optimal surface morphology of polypyrrole to maximize the gas-polymer interaction. Third, the substrate nature of the optical fiber has been changed to hydrophilic and hydrophobic, since this has an influence on the electronic and optical properties of polypyrrole deposited on it. Forth, incorporation of Cu^{2+} ions in the doped polypyrrole structure is studied. The best dopant, processing technique and substrate
nature are selected and investigated for sensitivity to DMMP. The sensing element length and diameter show a dramatic influence on the sensor response.

5.2 Sensor Operating Principle

The principle of operation of the optical fiber sensor is based on the intensity modulation induced within multimode optical fibers. The passive cladding of the fiber is replaced by a chemically sensitive cladding i.e. conducting polymer polypyrrole. As seen form section (4.6.1), polypyrrole shows a change in conductivity when exposed to DMMP. This will result indirectly in the change of the material refractive index. In this work a thin film of polypyrrole is coated on an optical fiber by in-situ deposition and monomer vapor phase deposition methods. The refractive index of polypyrrole is measured by ellipsometry. The complex refractive index of polypyrrole is given by eq. 5.1

$$n_{\text{clppy(complex)}} = n_{\text{clppy}} + ik_{\text{clppy}}.$$  (5.1)

Where $n_{\text{clppy(complex)}}$ is the complex refractive index of the polypyrrole cladding

$n_{\text{clppy}}$ is the real part of refractive index of the polypyrrole cladding

$k_{\text{clppy}}$ is the complex part of refractive index of the polypyrrole cladding

The real part ($n_{\text{clppy}}$) governs the light propagation through the sensing element, and the complex part ($k_{\text{clppy}}$) governs the light absorption in the thin film. The complex refractive index change due to chemical adsorption causes a change in the propagation as well as absorption of light through the modified section causing intensity modulation through the optical fiber sensor. Fig. 5.1 shows the schematic of the fiber sensing region. As seen from the Fig. 5.1 the light incident on the
core/polypyrrole interface refracts into the polypyrrole cladding because of higher refractive index of polypyrrole relative to the refractive index of the core. The light is then reflected back in the core at the polypyrrole/air interface. The optical characterization of the fiber sensing element region is evaluated using the complex refractive index \( (n_{clppy} + ik_{clppy}, 1.8435 + i0.06768) \) of polypyrrole at 632.8nm, obtained from ellipsometry and thin film transmission experiments.

The refractive angle \( (\theta_{rpppy}) \) at the core/polypyrrole interface is calculated by the Snell’s law when light is incident at 81.28° (critical angle at the interface of the core/original cladding). The critical angle \( (\theta_{cpppy}) \) at the polypyrrole/air interface is calculated before and after DMMP exposure. The intensity ratio \( (I_r/I_i) \) of the reflected light \( (I_r) \) with the incident light \( (I_i) \) at the interface for one interaction is calculated.
according to the Eq. 5.2 given below, and the power loss coefficient T is given by Eq.5.3 [63].

\[
\frac{I_r}{I_i} = \frac{1}{2} \left[ \left( \frac{\tan(\theta_i - \theta_{rppy})}{\tan(\theta_i + \theta_{rppy})} \right)^2 + \left( \frac{\sin(\theta_i - \theta_{rppy})}{\sin(\theta_i + \theta_{rppy})} \right)^2 \right]
\] (5.2)

Where \( I_r \) Intensity of reflected light

\( I_i \) Intensity of Incident light

\( \theta_i \) angle of incidence on the modified cladding from the core (see Fig.5.1)

\( \theta_{rppy} \) angle of refraction in the modified cladding (see Fig.5.1)

\[
T = 1 - \frac{I_r}{I_i}
\] (5.3)

Where T Power loss coefficient

\( I_r \) Intensity of reflected light

\( I_i \) Intensity of Incident light

Table 5.1 provides the relations between \( \theta_{cppy} \), \( \theta_{rppy} \), \( I_i \) and \( I_r \) for various thin film structures. As it can be seen from the Table(5.1), there is a decrease in the refractive angle (\( \theta_{rppy} \)) at the core/polypyrrole interface after DMMP exposure, attributed to an increase in the real refractive index of polypyrrole upon DMMP exposure. The decrease in the refractive angle (\( \theta_{rppy} \)) leads to a further decrease in power loss coefficient, and also increases the number of interactions per unit length of the sensing element. This latter effect coupled with the observed increase in the absorbance of polypyrrole thin films upon DMMP exposure may lead to a decrease in the intensity of light through the sensing element after DMMP exposure. The absorbance parameter here is the complex part of the refractive index (\( k_{cppy} \))
The reversibility of the developed sensor depends on the chemical reaction between the polypyrrole and DMMP. After DMMP is removed, polypyrrole can recover in air due to DMMP desorption. The sensor can therefore be used as a reversible one in the case of DMMP sensing.

**Table 5.1 Optical parameters of the fiber modified region with in-situ deposited polypyrrole as modified cladding**

<table>
<thead>
<tr>
<th>Film State</th>
<th>Θ(_{rppy})</th>
<th>Θ(_{cppy})</th>
<th>I(_r/I_i)</th>
<th>T</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>As In-situ</td>
<td>59°</td>
<td>36.78°</td>
<td>0.28</td>
<td>0.72</td>
<td>0.06768</td>
</tr>
<tr>
<td>After DMMP exposure</td>
<td>56.5°</td>
<td>35.45°</td>
<td>0.32</td>
<td>0.68</td>
<td>0.07017</td>
</tr>
<tr>
<td>As Vapor deposited</td>
<td>50.3°</td>
<td>32.37°</td>
<td>0.36</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>After DMMP exposure</td>
<td>45.4°</td>
<td>29.71°</td>
<td>0.40</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

**5.3 Development of the Fiber Sensing Element**

The sensing element i.e. the modified cladding region, preparation involves two major steps, (a) removal of the passive cladding (fiber etching), and (b) application of active cladding (fiber coating). An all silica multimode fiber with core/cladding/jacket dimension of 105/125/250 µm was used in this work. A meter length of optical fiber is used and a small section (1cm-3cm) of the jacket is stripped off the center of the optical fiber.
5.3.1 Fiber etching

The exposed section of the fiber is immersed in HF (hydrofluoric acid) solution which etches and removes the glass cladding of the optical fiber. The etching process is shown in Fig. 5.2, while the fiber is immersed in the etching solution (HF) the fiber is connected to a He-Ne (wavelength 633 nm) light source and a Silicon photo-detector (Newport 818 SL wavelength range 400-1100 nm) and the power transmitted is continuously monitored. The optical power transmitted through the fiber remains constant as long as the glass cladding remains and there is a sudden drop in the power as the cladding is completely removed as seen in the etching plot in Fig. 5.3. A concentration of 16.3% HF takes 30 min to etch away a 10 micron thick cladding. Fig. 5.4 shows the optical micrograph of the etched surface of the fiber indicating uniform etching achieved by this method.

![Fig 5.2 Schematic showing the fiber etching setup](image_url)
Fig 5.3 Etching plot showing the light intensity as the fiber is etched using a 16.33% HF solution.

Fig 5.4 Optical micrograph of the optical fiber, (a) etched section (b) gradual change of the interface region between the etched and unetched part.
5.3.2 Fiber coating

**In-situ deposition of polypyrrole**

The in-situ deposition of the chemically active polypyrrole on the fiber modified section is achieved by suspending the etched region of the optical fiber in the oxidant solution a mixture of 100ml deionized water, 3.5g of FeCl₃·6H₂O (oxidant) and 1M dopant acid (HCl, NDSA or ASQA). The monomer solution which consists of a 100ml deionized water and 0.6ml of pyrrole monomer is then added to the oxidant solution with the fiber dipped, inside as shown in Fig. 5.5. After a few minutes the polymerization takes place and the solution turns from orange to black. Deposition takes place as the polymerization continues. The fiber is left in the polymerization process for 5 minutes and then is washed with deionized water to remove the residual oxidant.

**Monomer vapor phase deposition.**

In the monomer vapor phase deposition the etched section of the optical fiber is coated with the oxidizer FeCl₃·6H₂O by dip casting and then the oxidizer coated section of the optical fiber is exposed to pyrrole monomer vapor as shown in Fig. 5.6. The monomer vapor polymerizes around the optical fiber in contact with the oxidizer, a very thin and uniform layer of polypyrrole film is obtained on the etched surface.
Fig 5.5 Experimental setup for the fiber coating by in-situ deposition

Fig 5.6 Experimental setup for the fiber coating by monomer vapor deposition.
5.3.3 Testing of the optical fiber sensing element

The sensing elements prepared is cleaved at both ends to have mirror flat edges using the York F11 fiber cleaver, perfectly flat fiber edges gives optimal light coupling into the fiber. The cleaved sensor element is then integrated with a He-Ne (wavelength 633 nm) light source and a silicon photo-detector (Newport 818 SL wavelength range 400-1100 nm), the complete experimental set up is shown in Fig. 5.7. The sensing element is exposed to DMMP (dimethylmethylphosponate) vapor. The output intensity is recorded by a power meter (Newport 1815C power range 20nW-2kW), which is connected to an oscilloscope for real time measurement. The trigger mechanism consists of another LED - detector combination which cuts the light to the detector when the DMMP container comes under the sensing element and in between this LED and detector.

5.4 Results and Discussion

5.4.1 Sensor test

The sensor response to DMMP vapor exposure (without any added dopant) is shown in the Fig. 5.8. A percentage response of about 2.1% was obtained. This response is attributed to the leaking of the higher order modes through the modified cladding of the fiber, due to the increased conductivity in polypyrrole film due to DMMP adsorption. The percentage response was calculated using the equation given below
Fig 5.7 Experimental setup for sensor testing

\[
\% \text{ Sensor Response} = \left(\frac{I_{\text{out}} - I'_{\text{out}}}{I_{\text{out}}}\right) \times 100
\]  (5.4)

Where \(I_{\text{out}}\) is the average light intensity before gas exposure

\(I'_{\text{out}}\) is the average light intensity after gas exposure

DMMP, interacts with the conductive polymer to increase the quantity of free and mobile hole charge carriers. This results in an increase in conductivity, this conductivity change is brought about by a change the number of charge carriers increasing the absorbance and a change in the mobility of the charge carriers which increases the real part of the refractive index, and hence an increase in the complex refractive index of the coated polypyrrole.

5.4.2 Influence of dopants

The sensing elements were tested to note the influence of adding dopants to polypyrrole on the sensor response to DMMP. Three different dopants i.e. HCl, NDSA & ASQA were added during the polymerization stage and were coated for 5 min by in-situ deposition. The concentration of the dopant acid is varied (0.1ml,
0.5ml, 1ml, 1.5ml of 1M dopant solution in 100ml oxidant solution) to investigate the influence of doping concentration on the sensor response. The choice of the three particular dopants is made on the bases of their reported [7] sensitivities to DMMP. Figs. 5.9a-c are the waveforms obtained for 0.5ml of HCl, NDSA & ASQA doping to polypyrrole respectively. The upper waveform being the sensor response and the lower waveform being the trigger i.e. the start of the exposure of DMMP. It can be seen that the doping polypyrrole results in a dramatic change in the percentage sensor response form just 2.1% for undoped polypyrrole to 15.75% for HCl and NDSA doped and 4.21% for ASQA doped polypyrrole. This increase in the sensor response to DMMP in doped polypyrrole may be attributed to conformational changes which may come about in doped polypyrrole due to DMMP adsorption [57, 58]. These conformational changes may further increase the conductivity change upon DMMP exposure,
resulting in an enhanced sensor response. It is found that as the amount of dopant is increased the sensor response in the case of HCl & NDSA increases up to 0.5ml of 1M concentration and decreases as the dopant amount is increased further, for ASQA there is a gradual decrease observed, with increasing dopant concentration, Fig. 5.10. X-Ray Diffraction studies [64] indicate an

![Graph](a)
![Graph](b)
![Graph](c)

Fig. 5.9 Sensor Response for Doped Polypyrrole for (a) HCL, (b) NDSA, (c) ASQA dopants.
Fig. 5.10 Influence of dopant concentration of the sensor response

increase in crystallinity of the polymer when the primary NDSA doping is increased. This increased crystallinity at higher doping concentrations may be responsible for lower sensor response. The best response time (6 sec) is observed in the ASQA (0.5ml) doped sample but the sensor response is low (4.03%) as compared to the other two dopants i.e. NDSA & HCL which give a sensor response of (15.75%), Fig. 5.11. The optimal dopant and dopant concentration is 0.5 ml of 1M NDSA in 100ml oxidant solution with a sensor response of 15.75% and a response time of 7 sec.
5.4.3 Influence of polymer processing

The ESEM analysis of the surface morphology of polypyrrole processed by both in-situ and monomer vapor phase deposition is shown in Fig. 5.12a&b. As seen from the ESEM micrographs the polymer processed by the in-situ deposition process Fig. 5.12a shows a highly porous microstructure with pore sizes ranging from 1-1.5 µm. This kind of a coating microstructure is advantageous from the sensor point of view since
this kind of microstructure provides a large surface area of interaction between the analyte and polymer. The mechanical adhesion of the polymer coating to the optical fiber is not strong, so long term mechanical stability of the coating is a factor for concern.

Fig. 5.12 ESEM micrographs showing 12000X high magnification surface morphology of (a) in-situ deposited polypyrrole, (b) monomer vapor phase deposited polypyrrole.

Fig. 5.13 ESEM micrographs showing 150X low magnification surface morphology of coated fiber (a) in-situ deposited polypyrrole, (b) monomer vapor phase deposited polypyrrole
On the other hand the coating microstructure obtained by the monomer vapor phase deposition has a low porosity with pore size ranging from 0.1-0.2 µm which is an order of magnitude less than the pore size obtained by the in-situ deposition Fig. 5.12b.

The coating quality and adhesion to the fiber is much superior to the one obtained by in-situ deposition. Fig. 5.13a-b shows the low magnification SEM micrographs for optical fiber coatings for the in-situ and monomer vapor phase deposition respectively, monomer vapor phase deposition clearly shows a much uniform deposition. The reason for

![Sensor response graphs](a) (b)

Fig. 5.14 Sensor response for NDSA doped polypyrrole using (a) in-situ deposition, (b) monomer vapor phase deposition.

obtaining a much uniform coating in the case of monomer vapor phase deposition is that in this case the polymerization takes place on the surface of the fiber where as in the in-situ deposition the polymerization takes place throughout the solution so there
is a lot of random deposition of oligomers from the solution onto the fiber. Fig. 5.14a&b compare the sensor response obtained for the in-situ (15.75%) and monomer vapor phase deposition (3.0%) for the NDSA doped polypyrrole, shows the clear advantage of having high porosity for sensor response.

5.4.4 Influence of processing time

As the deposition time of polypyrrole on the fiber is increased from 5 min to 12 min, the sensor response shows a dramatic decrease from 0.18 for a 5 min deposition down to almost zero for a 12 min deposition, as seen from Fig. 5.15. This decrease in the sensor response was analyzed by measuring the pore size of the developed polymer microstructure, the thickness of the deposited film, and using ESEM.

Fig 5.15 Sensor response dependence on in-situ deposition time of polypyrrole.
The ESEM micrographs in Fig.5.16a-5.18a show the high resolution polypyrrole microstructure of 5min, 7min and 10min in-situ deposition on the etched fiber. These micrographs were used to measure the pore size of the deposited polypyrrole microstructure. The measured pore sizes were 0.37, 0.631, 0.808 & 1.12 microns for 5, 7, 10 and 20 min deposition respectively, Fig. 5.19. From the high resolution ESEM study it is observed that as the deposition time is increased the pore size increases. This high porosity at longer deposition times allows a much larger surface area of interaction between the analyte (DMMP) and polymer (polypyrrole), but inspite of the increased porosity with deposition time a decrease in the sensor response is observed.

To explain the above decrease in the sensor response with increased deposition time, lower resolution ESEM microscopy was performed on the samples to calculate the film thickness on the fiber. The ESEM micrographs shown in the Fig. 5.16b-5.18b, suggest that there is a dramatic increase in the coating thickness i.e. 10, 70, 170, 228 microns for deposition times 5, 7, 10 and 20 min respectively, Fig. 5.20. This increased thickness of the coating at longer deposition time, increases the analyte diffusion time into the coating to the core-modified cladding interface. This effect may limit the sensor response at longer deposition times.
Fig. 5.16 ESEM micrograph showing (a) 15000X & (b) 150X Magnification image of a 5 min in-situ deposited polypyrrole on etched optical fiber substrate.

Fig. 5.17 ESEM micrograph showing (a) 15000X & (b) 150X Magnification image of a 7 min in-situ deposited polypyrrole on etched optical fiber substrate.
Fig. 5.18 ESEM micrograph showing (a) 15000X & (b) 100X Magnification image of a 10 min in-situ deposited polypyrrole on etched optical fiber substrate.

Fig 5.19 Polypyrrole microstructure pore size dependence on in-situ deposition time.
Fig 5.20 Polypyrrole coating thickness dependence on the in-situ deposition time

5.4.5 Influence of substrate nature (Hydrophobic or Hydrophilic)

The rational for treating the substrate hydrophobic or hydrophilic was based on the reported polypyrrole morphology dependence on the substrate nature. The reported film morphology on hydrophobic surfaces consists of a continuous granular matter while the films on the hydrophilic surfaces consist of spheres [65-66] as shown in Fig.5.21. This difference results in varied electrical properties of polypyrrole.

The etched fiber surfaces were made hydrophilic by immersing them in a “piranha solution”, which is prepared by mixing concentrated H₂SO₄ and 30% H₂O₂
in a 2:1 v/v ratio. The optical fibers were immersed in this hot solution for around 1 hour and rinsed with deionized water. For the hydrophobic treatment the fibers were immersed in a solution that is a mixture of a 100ml of hexanes and 0.5ml of octadecyltrichlorosilane, C_{18}H_{37}SiCl_{3}. The fibers were kept submerged into the solution for about 30 seconds to render them hydrophobic. The treated surface was then coated with polypyrrole by insitu deposition. The Fig. 5.22a-b show the waveforms obtained for the 0.5ml 1M NDSA doped polypyrrole. It can be seen that the hydrophobic substrate gives an almost similar sensor response as hydrophilic substrate. The ESEM micrograph for the polypyrrole deposited on both hydrophilic and hydrophobic substrates is shown in fig (5.23a&b) respectively.

Fig. 5.21 SEM micrograph showing the surface morphology of polypyrrole deposited on hydrophilic(A) and hydrophobic(B) substrates[66].
Fig. 5.22 Sensor response for NDSA doped polypyrrole using (a) Hydrophilic substrate, (b) Hydrophobic substrate.

Fig. 5.23 ESEM Micrographs showing surface morphology of polypyrrole deposited on (a) hydrophilic, (b) hydrophobic glass substrate.

While the final response is the same, we can see that the Fig 5.22a i.e. for hydrophilic substrate shows a faster response than Fig 5.22b i.e. for hydrophobic substrate, this is because higher porosity is observed in the polymer deposited on hydrophilic substrate, see Fig 5.23a than the one on hydrophobic substrate, see Fig 5.23b.
5.4.6 Influence of metallic ions

Kepley et al. [67] have established enhanced sensitivity to organophosphates to surfaces treated with Cu$^{2+}$. The rational for the addition of metallic copper ions in the polymer structure is that, Cu$^{2+}$ and some of its chelates are hydrolysis catalysts for nerve agents. Unsaturated Cu$^{2+}$ is thus expected to provide with selective and reversible binding sites for organophosphates. Fig. 5.24 shows the surface binding and desorption scheme of organophosphates on a composite monolayer consisting of Cu$^{2+}$ ions.

![Chart I](chart.png)

Fig. 5.24 Surface binding and desorption scheme of organophosphates on a composite monolayer consisting of Cu$^{2+}$ ions.

Optical fiber sensing elements were processed using NDSA doped polypyrrole as modified cladding and the coated section was dipped in 1M Cu(ClO$_4$)$_2$.6H$_2$O (Copper(II) perchloride hexahydrate) solution. The sensor response obtained for the treated fiber sensors is shown in Fig. 5.25. The response obtained for Cu$^{2+}$ treated sensing elements exposed to 26ppm of DMMP is much enhanced.
(25.75%) than the regular untreated fiber (15.75%), which is attributed to the specific Cu$^{2+}$ DMMP binding sites which may have formed in the polypyrrole structure.

![Graph showing sensor response](image)

**Fig. 5.25** Sensor response for NDSA doped polypyrrole with Cu$^{2+}$.

### 5.4.7 Sensitivity

The sensing element prepared by the insitu deposition technique, deposited on an etched fiber surface doped with 1M NDSA polypyrrole as sensing material shows the maximum sensor response to room temperature vapor pressure (about 0.1mm Hg, 134 ppm) of DMMP. This sensing element was then used for sensitivity study by lowering the concentration of DMMP by injecting dilute vapors of DMMP. The vapor dilution was achieved by mixing room temperature vapor of DMMP with dry air in a syringe, as shown in Fig. 5.26. This dilute vapor was then introduced in the sensing chamber for sensitivity study. The sensor intensity change response obtained for the lower concentrations is shown in Fig. 5.27. These responses reveal that the sensing element can be made sensitive to concentrations as low as 26ppm which corresponds to 80% dilution.
Fig. 5.26 Schematic of the experimental setup for sensor DMMP sensitivity study of room temperature vapor of DMMP. Which is more sensitive than the reported chemiresistor devices which sense DMMP using polypyrrole as their sensor element [7, 51].

Fig. 5.27 Sensor response of NDSA doped polypyrrole to various concentrations of DMMP, A: Boiling point vapor, B: Room temperature vapor (134ppm), C: 60% dilute vapor (80ppm), D: 40% dilute vapor (53ppm), E: 20% dilute vapor (26ppm).
5.4.8 Influence of sensing element length

Two different sensing element lengths i.e. 1cm and 3cms, were etched and coated in-situ by NDSA doped polypyrrole. Fig. 5.28 shows the sensor response for both the sensing elements. As seen from the sensor response there is a 15.75% response in intensity for the 1cm long element where as a 41.17% response for a 3cm long sensing element when exposed to 134ppm of DMMP. The decrease in light intensity is attributed to the increase in the number of leaky modes and absorbance of the NDSA-doped polypyrrole films due to the increase in the refractive index in the films due to DMMP adsorption, as observed in the ellipsometry, and decrease in the thin film transmission, due to DMMP adsorption. The increase in the percentage sensor response due to the increase in the sensing element length from 1cm to 3cm can be explained by the three fold increase in the number of interactions between the core and cladding interface of meridional rays as shown in the Fig. 5.29.

![Sensing element length graph](image.png)

Fig. 5.28 Sensor response to DMMP for sensing element length 1cm and 3cm.
The number of meridional ray interactions ($N_m$) at core – cladding interface is given by eqn(5.5)

$$N_m = \left\{ \frac{L \tan \phi_r}{2a} \right\}$$

where

L fiber length

a core diameter

$\phi_r$ refractive angle in the fiber

The Fig. 5.30 shows a plot of the number of meridional ray interactions at the core-cladding interface ($N_m$) and the sensing element length. It is seen from the linear plot Fig. 5.30 that there is a three fold increase in these interactions which may be responsible for the almost three fold increase in the percentage sensor response obtained by changing the sensing element length from 1cm to 3cm.
5.4.9 Influence of fiber diameter

The sensing element region was over etched into the core to investigate the influence of over-etching on sensor response. Fig. 5.31 shows the sensor response obtained for 105 microns, 96 microns and 93 microns respectively,

![Graph showing linear rise in number of meridional ray core cladding interactions as the sensing element length is increased.](image)

105 microns being the core diameter. It is seen that the sensor response due to over etching 9 to 12 microns into the core results in an increase of percentage response from 15.75% for the 105 micron diameter to 21.19% and 42.68% for the 96 microns and 93 microns respectively. This increase in the sensor response may be attributed to the increase in the number of leaky modes interacting with the modified cladding due to a decreased core diameter. Also there is an increased electric field in the absorbing cladding due to an increase in the $E_0$ factor in eq. 5.6 as the core diameter decreases in the sensing region.

$$E = E_0 \exp\left(-\frac{(r-a')}{d_p}\right)$$  \hspace{1cm} (5.6)
Where

$E_o$ is the electric field at the core cladding interface

$a'$ is the effective core radius after over etching

$d_p$ is the evanescent field depth.

![Influence of over etching](image)

Fig. 5.31 Sensor response to DMMP for fiber core diameters 105, 96, 93 microns.

5.4.10 Influence of light source intensity

The influence of light intensity on sensor response to DMMP was investigated using a 15mW He-Ne laser (632.8nm). The sensor response obtained for light power 1mW, 2mW, 3mW and 4mW is shown in Fig. 5.32. The percentage response for the sensors show a maximum for the 3mW power i.e. 19% which reduces to 10% when the light power is 4mW as compared to 15.75% for 1mW and 11% for 2mW as seen in Fig. 5.33. The reason for this decrease in the sensor response is not clear at the moment, but at higher light powers we suspect some material degradation of the polypyrrole due to sensing element heating which may deteriorate the sensor response. More future work is needed to investigate the effect of heating on the polymer polypyrrole as an optical waveguide.
Fig. 5.32 Sensor response to DMMP for light intensity 1, 2, 3 and 4 mW respectively.

Fig. 5.33 Influence of light intensity on the percentage sensor response.
5.5 Sensor Issues

5.5.1 Selectivity

Selectivity of the developed sensor towards DMMP is a very important issue and needs to be addressed. It is known that polypyrrole films show electronic changes when exposed to vapors like ammonia, hydrogen-peroxide, organic vapors like acetone and methanol. The developed sensor was tested for its cross sensitivity to other potential analytes like ammonia, acetone, methanol, and water vapor. Fig. 5.34 shows the percentage sensor response data on the sensor test. Though there is negligible intensity change of 0.4% in the presence of water vapor there is an observed intensity decrease of 4.2 % upon ammonia exposure and an intensity increase of 3.8 % and 2.8% upon exposure to acetone and methanol respectively. These responses are attributed to the polypyrrole swelling upon exposure to acetone and methanol [68] and the primary doping to polypyrrole when exposed to ammonia [69]. Kepley et al [67] have established enhanced selectivity and sensitivity to organophosphates to surfaces treated with Cu$^{2+}$. The rational for the addition of metallic copper ions in the polymer structure is that, Cu$^{2+}$ and some of its chelates are hydrolysis catalysts for nerve agents. Unsaturated Cu$^{2+}$ are thus expected to provide with selective and reversible binding sites for organophosphates. Optical fiber sensing elements were processed using NDSA doped polypyrrole as modified cladding and the coated section was dipped in 1M Cu(ClO$_4$)$_2$.6H$_2$O (Copper(II) perchloride hexahydrate) solution. The response obtained for Cu$^{2+}$ treated sensing elements is much enhanced (25.75%) than the regular untreated fiber (15.75%), which is attributed to the specific Cu$^{2+}$ DMMP binding sites which may have formed
in the polypyrrole structure. We have obtained a 5 fold increase in the percentage response for DMMP when treated with unsaturated Cu$^{2+}$ ions as compared to other gases, this difference in the response amplitude may be used to selectively distinguish DMMP from other potential analytes which react with polypyrrole producing a much lower sensor response.

![Graph of sensor response for DMMP, ammonia, acetone, methanol, and water.](image)

Fig. 5.34 Percentage sensor response for sensor test with analyte DMMP, ammonia, acetone, methanol, and water.

### 5.5.2 Reversibility

The sensor reversibility is studied by exposing the sensing element to DMMP then letting it recover in ambient air, and again exposing it to DMMP. The sensor response for the reversibility study is shown in the Fig. 5.35. As seen from the figure
the sensor developed shows partial reversibility towards DMMP. The light intensity recovery after 1st exposure is 97.8 % and 96.3% after 2nd exposure of the original intensity. The partial recovery of the light intensity may be attributed to the partial de-adsorption of the DMMP molecules from the surface of the sensing element leading to refractive index decrease.

Fig. 5.35 Sensor response for reversibility study by repeated exposure of DMMP to sensing element

5.5.3 Thermal & environmental stability

The light transmission through the fiber sensing elements were tested for the influence of temperature. Fig. 5.36a show the light power transmission decrease as the temperature is increased from room temperature (25°C) to (50°C). Four probe resistivity measurements were conducted on the polypyrrole thin films, shown in Fig. 5.36b. This decrease in output power is attributed to the decrease in the resistivity of doped polypyrrole films upon temperature increase [70-72]. Thermal stability of the
polypyrrole films is reported to have improved by incorporation of aromatic dopants such as anthraquinone-2-sulphonic acid in polypyrrole [73].

The environmental stability study was performed by aging the polypyrrole thin films and sensing elements over a period of 5 weeks and constantly monitoring the sensor response and the resistivity of polypyrrole. The four probe technique was used to measure the sheet resistance of the polypyrrole films deposited on glass slide by in situ deposition. The aging was performed at room temperature (25°C) and at a 30% relative humidity. A constant sheet resistance increase in the polypyrrole films was observed over a period of 21 days as seen in Fig. 5.37a. This decay of conductivity in polypyrrole films is attributed to the oxidation of the polymer backbone, resulting in a reduction of the conjugation length, hence a decrease in conductivity. The sensor response is observed to decrease from 15.75% overnight to 3.7% for a five week aging process, Fig. 5.37b. This decay of the sensor response may be attributed to the decay in the resistivity of the polypyrrole films due to aging. Addition of 2,4-dihydroxybenzophenone in the polymerization mixture results in a reported enhancement of the stability of the films at ambient conditions [74].
Fig. 5.36 (a) Light intensity through the optical fiber as the temperature is increased from 25 to 50°C respectively, (b) Sheet resistance decay as the temperature is increased of polypyrrole thin films from 25 to 55°C.

Fig. 5.37 (a) Sensor response for 1, 3 and 5 weeks of ambient aging of the sensing element, (b) Sheet resistance measurements on aging polypyrrole thin films.
5.6 Conclusion

This chapter reports the work done on the coated modified section of the fiber to enhance the sensor sensitivity. There are several parameters that are investigated w.r.t. the sensitivity of polypyrrole as a chemochromic material applied as a modified cladding to the optical fiber.

a) Chemical doping of the polymer with three different dopants i.e. HCl, NDSA and ASQA and the influence of concentration of the dopants is investigated. From the sensor sensitivity and response time point of view NDSA showed the best result with a percentage sensor response of 15.75% and a response time of 7 sec for a concentration of 134 ppm DMMP.

b) Processing of the polymer to have control over the surface morphology of the polymer, to control the interaction area between the analyte and the polymer. Two processing techniques are compared i.e. in-situ deposition and monomer vapor phase deposition. The SEM and ESEM characterization study revealed that the polymer deposited by in-situ deposition has a nonuniform but highly porous coating which gives a highly sensitive but a weakly adhesive coating, the monomer vapor deposition technique on the other hand gives a strongly adhesive but a less sensitive coating due to less porosity and small pore size.

c) The effect of substrate nature of the etched fiber is investigated by modifying it to hydrophilic or hydrophobic. This substrate treatment did not result in any
difference in sensor response, as there were small morphology differences observed from ESEM microscopy study.

d) The addition of Cu$^{2+}$ ions to the NDSA doped polypyrrole structure increases the sensor response from 15.75% to 25.75%, this increase is attributed to the DMMP selective binding sites in polypyrrole structure.

e) The optimal sensing element is the one deposited of as received fiber surface with NDSA doped polypyrrole coated by the insitu deposition technique. The sensitivity of the developed composition and morphology shows sensitivity down to 26 ppm of DMMP, which is much lower than the already developed amperometric sensors [7].

f) High percentage sensor responses can be obtained by increasing the length and decreasing the diameter of the sensing element region.

g) Increasing the light intensity may result in heating the sensing element region and decrease in the sensor response.

h) Selectivity of the developed sensor poses serious issues of false alarm due to other gases like ammonia and acetone. To an extent, the sensor can be made selectively sensitive to DMMP by addition of unsaturated Cu$^{+2}$ ions in the polymer structure. Future work needs to be done to solve this issue. A
proposed method would be to multiplex other sensors sensitive selectively to these other gases with the developed sensor to nullify the false alarm.

i) The developed device shows poor environmental and thermal stability which may be improved by addition of conductivity stabilizers in the polypyrrole structure.

The next chapter 6 presents the issue of mechanical durability of the sensor device developed in this chapter. The mechanical property of polypyrrole is studied using the nanoindentation technique and the adhesion between the polypyrrole film and the fiber surface is investigated and reported.
CHAPTER 6: MECHANICAL PROPERTY AND ADHESION OF POLYPYRROLE THIN FILMS.

6.1 Introduction

The intrinsic mechanical properties of polypyrrole and quality of adhesion between the polypyrrole films and optical fiber are important factors for the mechanical durability of the fiber sensor. It can be seen from the section (5.4.3) of chapter 5 that the mechanical property of the polypyrrole coating on the fiber obtained from the in-situ deposition technique is very poor in terms of integrity and adhesion of the films on the fiber surface. This chapter covers the mechanical property measurement and adhesion measurement of polypyrrole films on glass substrates. The intrinsic mechanical property of the polypyrrole film is measured using the nanoindentation technique. The adhesion between the polypyrrole films and substrate is enhanced by treating the glass substrate with silane coupling agent and by increasing the roughness of the substrate surface. The adhesion of the polypyrrole films on glass substrate is measured using the ASTM-4541 pull off test method. DMMP sensor tests are conducted on polypyrrole films deposited on silane treated and rough optical fibers to note the influence of these adhesion enhancement techniques on the sensor sensitivity to DMMP.

6.2 Nanoindentation

Nanoindentation is simply an indentation test in which the length scale of the penetration is measured in nanometers ($10^{-9}$). The nanoindenter made by MTS Corporation was used in this work. The load-displacement resolutions are reported to be 50nm and 0.004nm respectively for this instrument. This instrument applies load
by a calibrated electromagnetic coil and displacement of the indenter is measured by a capacitive plate transducer. The general schematic of this instrument is shown in Fig. 6.1. The Berkovich indenter was used for the testing, a berkovich indenter is a hard tip, typically made of diamond. Fig.6.2 shows a very high resolution SFM (Scanning force microscopy) image of a Berkovich indentor tip [74]. During the indentation test the Berkovich indentor tip is pressed into the sample with a known load. After some time, the load is removed. The area of the residual indentation in the sample is, measured and the hardness H, is defined as the maximum load, P, divided by the residual indentation area, A, given by Eq. 6.1,

\[ H = \frac{P}{A} \]  

(6.1)

The residual indentation area for the berkovich tip is given by eq. 6.2 [75],

\[ A = 3(3^{1/2})h_p^2 \tan^2 \theta \]  

(6.2)

Where \( \theta = 65.3^\circ \) (semi-angle for berkovich indentor)

\( h_p \) plastic depth of penetration.

Hence using Eq. 6.1 for Berkovich indenter the hardness is given by Eq. 6.3,

\[ H = \frac{P}{(24.5h_p^2)} \]  

(6.3)

The elastic modulus S of the sample is determined from the slope of the unloading of the load depth response as shown in Fig. 6.3.
Fig. 6.1 Nanoindentation machine set-up overview.

Fig. 6.2. Scanning force microscopy image of a Berkovich indentor tip
6.2.1 Nanoindentation results

A typical quasi-static load-displacement curve is shown in Fig. 6.3 for a typical polymer material. As the load is increased, the indenter sinks into the material due to both elastic and plastic deformation. If the load is held constant, the indenter continues to sink into the material due to time-dependent deformation (creep). When the indenter is unloaded, the material recovers by a process that is primarily elastic.

![Nanoindentation Curve](image)

Fig. 6.3. A typical nanoindentation curve for a polymer material.

![Nanoindentation Data](image)

Fig. 6.4. Load-displacement curve for polypyrrole thin film on glass substrate.
Table 6.1 Mechanical properties of glass substrate and polypyrrole film deposited in-situ on glass substrate

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Modulus (GPa)</th>
<th>Hardness (MPa)</th>
<th>Max Load (mN)</th>
<th>Max Depth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Substrate</td>
<td>65.25</td>
<td>6.9 (GPa)</td>
<td>0.25</td>
<td>24</td>
</tr>
<tr>
<td>Ppy Thin film</td>
<td>2.347</td>
<td>32 (MPa)</td>
<td>0.25</td>
<td>499</td>
</tr>
</tbody>
</table>

The Fig. 6.4. shows the load displacement curve for a polypyrrole film deposited on glass substrate. The result shows a load-displacement curve for a typical polymer material. Table 6.1 lists the results of the mechanical properties obtained for the substrate i.e glass slide and the polypyrrole thin film deposited in-situ on this substrate.

As seen from these results the glass substrate shows the observed mechanical properties of glass with a perfectly elastic load-displacement curve. The polypyrrole thin film shows a viscoelastic-plastic response with a modulus of 2.347 GPa which is comparable to the reported value of 2.5 GPa for polypyrrole thin films.

6.3 Adhesion

The term adhesion simply means sticking together of two similar and dissimilar materials [76]. The mechanism of adhesion between surfaces can be explained by six different theories: Physical adsorption, chemical bonding, diffusion, electrostatic, mechanical interlocking and weak boundary layer theory [77].
**a. Physical Adsorption:**

Physical adsorption between two surfaces in contact occurs because of the van der Waals forces across the interface, which involves the interaction between permanent and induced dipoles on the surface. An expression of these dispersion forces between molecules is given by the Eq. 6.4 below [77]

\[ E_{pa} = -\frac{2\mu_1^2\mu_2^2}{3kT(4\pi\varepsilon_0)^2r^6} \]  

(6.4)

Where \( E_{pa} \) is the potential energy for vander waals interaction

- \( \mu_1 \) and \( \mu_2 \) are the dipole moments
- \( r \) distance separating these dipoles
- \( \varepsilon_0 \) is the permittivity of free space
- \( k \) Boltzmann’s constant
- \( T \) absolute temperature

As seen from the equation above the potential energies of these interactions is inversely proportional to the 6\(^{th}\) power of the distance of separation these adhesive forces are only felt by the molecules on the topmost layer of the surface.

**b. Chemical Bonding**

Chemical bonding type adhesion between two surfaces involves the formation of a covalent, ionic or hydrogen bond across the interface of two surfaces. The energy of interaction for a covalent bond is given by the Eq.6.5 below [77]

\[ E_{cb} = \frac{z_1z_2e^2}{4\pi\varepsilon_0\varepsilon_r r} \]  

(6.5)
Where $E_{cb}$ is the potential energy of interaction between two ions

$z_1e$ and $z_2e$ are ionic charges

$\varepsilon_r$ is the relative permittivity of medium

$r$ is the distance between ions

An example of chemical bonding adhesion is the reaction of epoxide adhesive with a surface containing amine group to give C-N bond (291 kJ mol$^{-1}$). There is also evidence [76, 77] that covalent bonds are formed when silane coupling agents are used between two surfaces as explained in the section below.

c. Mechanical Interlocking

If one or both the surfaces are irregular then the adhesive or thin film can penetrate in these irregularities and form interlocking, increasing the adhesion between the two substrates.

d. Diffusion Theory

The diffusion theory considers the point that atoms or molecules of the surface may diffuse into each other at elevated temperature resulting in bonding or adhesion between two surfaces.

e. Electrostatic Theory

This theory explains the origin of adhesion between two metals kept in contact and develops an electrical double layer giving rise to a force of attraction.
Adhesion of polymer films on glass substrates can be enhanced by several ways and the various theories that explain the adhesion between two surfaces is explained above. In this work we exploit the chemical and physical adhesion enhancement between two surfaces to improve the adhesion between polypyrrole thin films on glass substrate.

6.4 Chemical Enhancement

6.4.1 Silane coupling agent

Silane coupling agents have shown to chemically react with the substrate and thin film to form chemical covalent bond across the interface. The silane coupling agent has the following structure

\[ R' \text{-Si-R}_3 \]

Where

R’ is the reactive group (will react with thin film)

R₃ is usually a methyl or ethyl group

During hydrolysis in water, the following reaction occurs:

\[ R' \text{-Si-R}_3 + 3\text{H}_2\text{O} \rightarrow R' \text{-Si-(OH)}_3 + 3\text{RH} \]

When this aqueous solution of silane comes in contact with an inorganic substance, the silanol is adsorbed by hydrogen bonding between surface hydroxyl groups and silanol groups as shown in Fig.6.5 the reactive group (R₃) on the silane agent then reacts with the adhesive (polymer film in this work) to form a covalent bond.
6.4.2 Roughness

Increasing the substrate roughness can cause an increased adhesion between the films and substrate. This happens because there is an increased surface area of contact between the film and the substrate leading to increase in van der Waals forces of attraction on the surface, increasing the surface roughness can also lead to mechanical interlocking between polymer molecules and the substrate leading to enhanced adhesion. Some simple cases of good and poor adhesion upon substrate roughening are shown in Fig. 6.6.
6.5 Adhesion Testing

Adhesion testing was performed using the ASTM D-4541 pull off test. The schematic of the test setup is shown in fig. 6.7. The test was conducted at a temperature and relative humidity of 20 °C, 65 % respectively. 12.7 mm [0.5 in] aluminum pull stubs [type PS-25 from M. E. Taylor Engineering, Inc.] were used with a 3M type DP-460 off-white adhesive [6 hrs curing time @ 20 °C.]. The thin films attached to the pull stub using the adhesive. These sample attached pull stubs were then attached to a fixture tailored for the pull off test. The self aligning fixture was coupled with testing fixture and integrated with instron for the measurement of force required for delamination of the thin film from
Fig. 6.7 Schematic of the set-up for the ASTM 4541 pull test

Fig. 6.8 Experimental set-up for measurement of delamination stress of polypyrrole films by the ASTM 4541 pull-off test
the substrate, shown in Fig. 6.8. The force to delaminate the thin film from the pull stub was recorded which was then converted to adhesive stress using the following Eq.6.6

\[
\sigma_{\text{delaminate}} = \frac{F_{\text{max}}}{\pi r^2}
\]

(6.6)

where

- \( F_{\text{max}} \) maximum force for delamination
- \( r \) radius of pull stub

6.6 Adhesion Results

6.6.1 Silane treatment

The pull off test was conducted on insitu and monomer vapor phase deposited samples on glass slides which were pretreated with aminopropyltriethoxysilane (APS). The results of the silane test, shown in Fig. 6.9 reveal that the delamination stress required for films deposited on substrates pretreated with silane are 2.245 and 2.387 MPa for insitu and monomer vapor phase deposited samples respectively as compared to 0.946 and 1.4386 MPa for insitu and monomer vapor deposited samples deposited on as received glass substrates. This enhanced adhesion between polypyrrole film and silane treated glass substrate is attributed to the bonding that may have formed between the film and substrate due to silane coupling agent [78][79].

The ESEM micrograph of polypyrrole films deposited on as received and pretreated glass substrates is shown in Fig. 6.10 a & b. These micrographs reveal that the surface folds seen on the films deposited on as received glass substrate are not
seen in the silane pretreated substrate indicating a more uniform morphology of polypyrrole films deposited on silane pretreated substrates.

The optical micrograph of a delaminated/intact interface of a film deposited on silane pretreated sample is shown in Fig.6.10 c & d. Incomplete delamination of the films is observed Fig.6.10d. this may result form incomplete silane coupling agent reaction between the film and substrate resulting in a reduced adhesion enhancement.

Fig. 6.9 Delamination stress results for polypyrrole deposited on glass substrates pretreated with APS.
Fig. 6.10. Microscopy of the delamination of polypyrrole films from glass substrates 
(a) Ppy film on as received glass, (b) Ppy film on silane treated glass slide, (c) 
delamination of the silane treated glass slide, (d) incomplete delamination of Ppy film 
deposited on silane treated glass slide.

6.6.2 Substrate roughness

The roughness of the glass slide substrates were increased by using polish 
papers 180 grid, 240 grid and 400 grid size. The results for these adhesion tests are 
shown in Fig. 6.11. It is apparent from the results that films deposited on glass slide
roughned by a coarse grid (180 Grid) takes a higher delamination stress i.e. 4.28 MPa, as compared to fine grid (240 Grid & 400 Grid) i.e. 3.31 & 2.14 MPa and a much lower delamination stress of 0.946 MPa for unpolished glass substrates, as shown in Fig. 6.11.

Fig 6.11. Delamination stress results for polypyrrole deposited on glass substrates roughened by a 400, 240 and 180 grid polish paper.
Fig. 6.12 Optical micrographs showing the interface of the delaminates/intact interface on polypyrrole films deposited on glass substrates roughened by (a) 180, (b) 240 and (c) 400 grid polish paper.

The increase in the adhesion due to surface roughening results from the fact that there is an increased surface area between the film and substrate and mechanical interlocking can also take place between the polymer molecules and the substrates due to surface roughness. This can be seen in the optical microscopy image shown in Fig. 6.12., no delamination is seen as the pull off stub is removed, indicating
penetration of the polymer particles in the grooves created when the substrate is roughened.

6.7 Mechanical Improvement and Testing of the Sensor

The adhesion testing results reveal that treating the glass slide substrate with silane coupling agent and increasing the roughness of the slide leads to better adhesion quality. The fiber surface is treated with silane coupling agent and the roughness of the fiber is increased to see how these changes influence the DMMP sensor response.

For silane treatment of the etched optical fibers the following 3 steps were performed

1) the etched section of the fiber was washed in distilled for 15 minutes
2) the fiber was washed in acetone for 10 minutes
3) Fiber was immersed in 2% solution of 3-aminopropyltriethoxysilane in acetone for 15 minutes.
4) Washed in distilled water and dried overnight.

For fiber roughness, the etched fiber was polished on a 400 Grid paper the use of coarse grid papers i.e. 240 & 180 grid leads to breakage of the fiber in the weak etched section. The sensor response is then measured by exposing the sensing element to DMMP, the procedure of this is explained in section (5.4.1). The sensor response results are shown in Fig.6.13.
Fig. 6.13 Sensor response for polypyrrole deposited on, As received, 400 grid roughened and APS silane treated optical fiber.

Fig. 6.14. Percentage sensor response for polypyrrole deposited on, As received, 400 grid roughened and APS silane treated optical fiber.
A marked decrease in percentage sensor response is observed from 15.75% for untreated fibers to 12% in 400 Grid rough fiber to a further drastic decrease to 2% for silane treated fibers as shown in Fig. 6.14. The 4% decrease in rough fibers may result, due to excessive scattering of light which is induced at a rough etched surface as shown in Fig. 6.15a. To explain the major decrease of 14% in silane treated fibers, the refractive index of the silane coating was determined using ellipsometry. The ellipsometry experiments reveal a refractive index of 1.35 for the silane layer that forms on the fiber surface between the polypyrrole film and fiber core. This refractive index of the silane coating is lower than that of the fiber core refractive index 1.45 which may lead to total internal reflection of the rays which would have otherwise served as leaky rays for sensing as shown in Fig. 6.15b. This may cause the marked decrease in the sensor response of silane treated fibers.

Fig 6.15 Schematic showing light and modified cladding interaction for (a) rough, (b) silane treated, optical fiber.
6.8 Conclusion

The mechanical property and adhesion measurement conducted on the polypyrrole films reveal three main points

1. The mechanical properties measurement yield a modulus of 2.37GPa which is consistent to the value 2.5 reported in literature.

2. The adhesion pull-off test performed on silane treated and rough substrate surface show an enhanced delamination stress of 2.245 and 2.14 MPa respectively as compared to 0.946 MPa samples deposited on as received glass substrates.

3. Enhanced film-substrate adhesion was achieved by silanation and roughness of the glass substrate, the sensor response decreased form 15.75% to 12% in case of rough fibers and to 2% in case of silane treated fibers.

The study conducted on mechanical properties and adhesion of polypyrrole thin films on glass substrates and the subsequent application of the adhesion enhancements to the optical fiber surface reveal that there is a trade off between improved mechanical property and the DMMP sensitivity of the device. As seen from the sensor response results there is a 4% to 14% decrease in the percentage sensor response when fiber etched surface is roughened and silane treated prior to polypyrrole deposition respectively.
CHAPTER 7: SUMMARY AND FUTURE WORK

7.1 Summary

This thesis reports successful development and application of doped polypyrrole films to on-fiber chemical sensor device to sense DMMP. The sensor design is based on modified cladding approach, where a doped polypyrrole film forms a modified cladding to an optical fiber.

The sensor principle is based on intensity modulation induced in the multimode fiber due to changes in refractive index and absorption in the polypyrrole modified cladding. Polypyrrole film shows a change in conductivity, refractive index and absorption when exposed to DMMP. DMMP brings about a change in the number and mobility of charge carriers in the polypyrrole backbone.

This thesis was developed in seven chapters which covered a literature review on fiber optic sensors which lead to the selection of modified cladding based sensors as a sensor design. The modified cladding design in optical fiber sensors provides an excellent design for this sensor development because of the high sensitivity and ease of fabrication of the sensor using this design.

Due to the reported sensitivity of polypyrrole thin films towards DMMP and its ease of synthesis and stability it is selected as the best candidate for application as a modified cladding to the above mentioned sensor design. Polypyrrole is
successfully synthesized in the form of thin films on glass and silicon substrates and characterized using Microraman and FTIR characterization techniques.

The DMMP sensing property of these polypyrrole thin films are established using the Four-probe technique for conductivity measurements, ellipsometry and thin film transmission measurements for real and complex refractive index during exposure to DMMP. These experiments clearly indicate that polypyrrole thin films show an increase in conductivity and an increase in refractive index when exposed to DMMP vapor. These optical property modulations that come about in thin films of polypyrrole and its ease of synthesis on the fiber make us select polypyrrole as a modified cladding to the optical fiber.

The application of polypyrrole on the optical fiber as modified cladding is done by etching the passive glass cladding of the optical fiber and coating the fiber with polypyrrole by in-situ or monomer vapor phase polymerization technique. This device is then integrated with a laser and detector and a data acquisition unit for the DMMP sensor test. The sensor response obtained at the preliminary stage shows a limited sensor response of 2-3% which is then enhanced by doping the polymer with HCl, NDSA and ASQA. NDSA showed the best result from the sensor sensitivity and response time point of view with a percentage sensor response of 15.75% and a response time of 7 sec for a concentration of 134 ppm DMMP. This dopant was used as a standard dopant to polypyrrole to investigate the effect of other properties as mentioned next on the developed sensor.
• **Coating process:** (a) insitu & (b) monomer vapor phase deposition to control the surface morphology of the polymer.

• **Substrate:** (a) hydrophilic & (b) hydrophobic for polymer morphology control.

• **Metallic Substitution:** Incorporation of Cu$^{2+}$ ions in polypyrrole structure is expected to provide selective and reversible binding sites for organophosphates.

• **Waveguide:** Influence of sensing element length and diameter.

• **Light Intensity:** Influence of light intensity through fiber.

• **Sensitivity:** Influence of concentration of DMMP.

• **Selectivity:** Sensor response to other gases.

• **Reversibility:** Sensor reversibility in terms of presence and absence of DMMP.

• **Thermal stability:** Sensor response due to temperature variations.

• **Durability (aging):** Influence of aging on sensor device.

The mechanical properties and adhesion of the polypyrrole film coated on the optical fiber are very poor and pose a serious issue regarding the mechanical stability of the developed device. The mechanical properties of the polypyrrole film deposited on the glass substrate were studied using the nanoindentation technique and the adhesion of the films were studied by pull-off testing of the thin films on the glass substrates. Adhesion enhancements were developed at the film/substrate interface as a result of silane coating and increased roughness.
The study conducted on mechanical properties and adhesion of polypyrrole thin films on glass substrates and the subsequent application of the adhesion enhancements to the optical fiber surface reveal that there is a trade off between improved mechanical property and the DMMP sensitivity of the device. As seen from the sensor response results there is a 4% to 14% decrease in the percentage sensor response when fiber etched surface is roughned and silane treated prior to polypyrrole deposition respectively.

7.2 Future Work

Inspite of the excellent results achieved on the sensitivity and response, more work is needed to enhance the sensor selectivity, environmental and thermal stability as well as sensor mechanical properties.

Selectivity: Selectivity of the developed sensor poses a serious issue giving rise to a false alarm situation. Future work need to be done by multiplexing the developed sensor with other sensor device selectively sensitive to gases like ammonia, nitrogen dioxide, acetone etc. to eliminate the false alarm situation. Also, study on the wavelength response for the other gases to select the proper light source which has a maximum response to DMMP and a minimum or zero response to other gases.

Environmental and thermal stability: Thermal stability of the polypyrrole films need further investigation, prolonged exposure to humidity may cause conductivity decay in the polypyrrole films which may be stabilized by Cu modification. Ambient
aging of the sensing polypyrrole films can lead to decay in conductivity, which may be stabilized by addition of 2,4-dihydroxybenzophenone at polymerization stage.

**Over mechanical property:** The mechanical property of the sensing element is weak, as it is a glass fiber of 100 microns diameter. This problem may be resolved by using porous cladding such as sol-gel glass clad embedded with polypyrrole. The porous coating in this region can permit the interaction of DMMP and polypyrrole.
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