6.1. Introduction

This chapter is focused on the development, characterization of PANI-HCl optical fiber ammonia sensor. The foundation of this sensor is based on the change of optical power or optical intensity modulation induced within modified multimode optical fibers. The sensor design is based on the modified cladding technique, i.e. the ammonia sensitive material; the conducting polymer film of the polyaniline doped with HCl, sensitive to ammonia gas with optimized synthesis parameters was coated on a small section of the uncladed fiber. The experimental results show a positive response of polyaniline coated optical fiber to ammonia vapor at room temperature. The polymer material, polyaniline was coated on uncladed fiber using in-situ chemical polymerization, which provides the porous surface morphology of polyaniline to maximize the gas-polymer interaction. The best dopant, processing technique and substrate nature were selected and investigated for better sensitivity to the ammonia. The sensing element length, source intensity and source wavelength, shows a dramatic influence on the sensor response.
In recent years, a lot of attention has been given to the use of conducting polymers in chemical sensors, as sensing layer for the detection of various gases, because it is easy for synthesis, consume less power and has low poisoning effect [1–8]. Conducting polymers are a new class of sensing materials, which can be prepared by a simple oxidative polymerization method. They exhibit reversible pH-induced spectroscopic and gas-induced conductivity changes. They also provide a suitable structure for immobilization of ligands, enzymes and antibodies. Therefore, their use in the development of novel chemical and biological sensors has received considerable attention [9-12]. The sensitive parameters in these sensors are changes in the work function, the conductivity or optical absorption coefficient of the polymer. Considerable effort has directed towards the development of chemical sensors by the change in optical properties [13-16]. Till now, metal oxides such as SnO$_2$ and Fe$_2$O$_3$ are mostly used as sensing materials. The principal disadvantages of such materials include high dependence on the detecting environments. However, the optical method shows independence from environmental interference. The polyaniline films show significant optical transmittance changes upon exposure to ammonia gas at room temperature. This study demonstrates the optical property advantage of polyaniline (PANI) over metal oxide. The method suggested in this work is the detection of a modulated signal caused by an absorbance coefficient variation. The interaction between the conducting polymer and gas molecules results in an increase or decrease of bipolaron densities inside the polymer band gap. Since the bipolaron excitations generally fall in the visible range, their population
modification implies both electrical and optical property changes in the conducting polymer [17]. Fiber optic sensors represent an exciting class of devices because of their lightweight, small size, low cost, immunity to electromagnetic interference, and ability to be embedded into other structures. The basic operation principle of the fiber-optic sensor is that when it is exposed to a chemical or physical stimulus, the intensity signal traveling through an optical fiber changes. Therefore, fiber-optic sensors provide a means whereby light guided within an optical fiber can be modified in response to external physical, chemical, biological, or other influences [18-22]. The fiber-optic sensor using cladding modification methodology is very attractive because of its large dynamic range, high sensitivity, and superior integration into other structures [23].

In this work, the low cost optical fiber chemical sensor, i.e. ammonia sensor is developed. The plastic (PMMA) optical fiber has been used for the sensing application. The fiber-optic sensing element is prepared by replacing the original cladding material with a chemical sensitive material, polyaniline, on a certain portion of an optical fiber. Initially, various process parameters viz. concentration of monomer, oxidants, doping acids, deposition time and reaction temperature have been optimized for the synthesis of PANI film on PMMA substrate, because PMMA material is being used for the fabrication of plastic optical fiber. Then the conducting polymer (PANI) with same optimized parameters was coated on uncladed portion of optical fiber. The gas sensing properties of the synthesized PANI film in terms of change in resistance of the
Development of PANI-HCl Optical Fiber…

film has been carried out by indigenously developed computer controlled gas sensing system. The optical properties of the sensor have been studied by indigenously developed optical fiber gas sensing chamber, when the sensor is exposed to the ammonia vapor. Light intensity modulation was achieved by this modified optical fiber structure based on the complex refractive index change of the cladding material when it was exposed to a chemical vapor. Polyaniline, representing a type of electronic polymer with conjugated polymer backbones, was selected as the modified cladding material because of its optical response when it is exposed to chemicals, such as ammonia and hydrochloride, and its flexibility, and readiness in processing ability [24-26].

Several components are required, in general, for the construction of a fiber-optic sensing set up: a light source, an optical focusing component, one or more optical fibers, a modulation sensitive mechanism, a photo detector, and signal processing components. For simplicity and minimizing cost, our sensing set up is illuminated with the light emitting diode (LED). The conducting polymer is uniformly deposited onto core (sensing region) of the optical fiber. In addition, the light transmitted through plastic optical fiber coated with the sensing layer is detected by photodiode. The light at the detector varies by adsorption of ammonia molecules into the conducting polymer surface. The light intensity at the detector changes with increasing gas concentration. As a result, the optical sensing method using a conducting polymer demonstrates possibility for application of gas detection. Therefore, employing light intensity variation at the detector stage, we have successfully developed an
optical ammonia gas sensor system, which is sensitive, easy to regenerate and inexpensive.

6.2. Theoretical part

The designing aspect of fiber optic sensor is as shown in Fig.6.1. The fiber optic sensor was designed by replacing the original passive cladding by a sensitive layer at sensing region. A three-step method was implemented to design the sensor. First, the plastic jacket was stripped. Second, the PMMA cladding layer was removed by combination of polishing with abrasive papers and application of the acetone and water on the fiber and polishing with the tissue. Third, a sensitive material was coated on the sensing region as a new cladding. The sensing mechanism is based on the interaction of the light transmitted in the optical fiber and an external chemical perturbation in the modified cladding region. This interaction results in the intensity modulation. The interaction between evanescent field (in the cladding) and external perturbation results in the attenuation of the guided light in the fiber core through absorption and fluorescence [27-30]. If the modified cladding has a higher refractive index than the core, a portion of guided modes is transferred to the radiation modes. In fact, the partial leaky-mode sensor was constructed which is based on the intensity modulation induced by the absorption of the refracted rays and evanescent field in the modified cladding. Since the modified cladding is very thin, the fiber-cladding layer is actually composed of two layers that are the modified material layer as the first and the air medium as the second layer.
Based on this type of the modified cladding structure, we expect that both the refracted rays and evanescent field within the cladding contribute to the sensor intensity modulation. Therefore, this fiber-optic sensor is assumed to be a partial leaky-mode type based on the existence of the multilayer modified cladding on the optical fiber. The total internal reflection condition would no longer exist in the modified region, where the modified fiber cladding has a higher refractive index than the core. However, as the modified cladding material is very thin, air medium acts as a second layer of the cladding. When a light ray interacts with the core/modified cladding interface, shown in Fig.6.1, part of the light is refracted into the cladding, and the other part of the light is reflected back into the core. The percentage of the light reflected back into the core depends on the refractive indices of core and modified cladding as well as the light incident angle. The light propagated inside the modified cladding is partially absorbed and the rest get refracted back into the core. When the light passes through the cladding, the light energy is attenuated which depends upon the absorption coefficient of the cladding material. The total energy loss after the light pass through the modified area depends on the light absorption by the modified cladding and the number of interactions between core and cladding. Fig.6.1 also shows that the guided ray does not interact with the core/modified cladding interface. However, the evanescent field of this type of the ray penetrates into the modified cladding. The power in the evanescent field is absorbed by the cladding, which also contributes to the signal modulation. Thus, the intensity modulation is caused by the attenuation of both the refracted ray
and the evanescent field in the modified cladding. High sensitivity, large
dynamic range, and quick response can be achieved by fine tuning of the
modified cladding properties.

Fig. 6.1 Configuration of fiber optic sensor and geometric optics ray through the
sensing region.

6.3. Experimental

6.3.1. Materials:

All chemicals used were of Analytical reagent (AR) grade. Aniline was
purchased from Rankem Ranbaxy New Delhi (India). Ammonium
peroxydisulfate was purchased from SpectroChem (India) and HCl was
purchased from Loba Chemie (India). Aniline was doubly distilled before use.

6.3.2. Instrumentation:

This part has already been discussed in chapter 5.
6.3.3. Synthesis of Polyaniline film by chemical polymerization

Aniline monomer was purified by distillation prior to use. All other reagents were of analytical grade and were used as received. PANI-HCl was synthesized using in-situ polymerization of aniline monomer by using ammonium peroxydisulfate (APS) as an oxidant in the presence of HCl as a dopant. The polymerization was carried out at 10°C ±0.5 in a temperature controlled water bath for 20 hour. In this process, 1 M of HCl aqueous solution and 0.25 M of aniline were added into 10 ml of distilled water, and (then) the solution was stirred by an electromagnetic stirrer for about half hour. Afterwards the solution was cooled down to 10°C and 10 ml of APS aqueous solution (0.25 M) was added drop wise to the solution containing HCl and aniline monomer with continuous stirring. The PMMA substrate was submerged in the reaction mixture of aniline and APS and as a result PANI film was deposited on PMMA substrate. Then the resulting film was removed from the solution, washed with distilled water and dried.

6.3.4. Preparation of optical fiber sensing element

Preparation of the sensing element i.e. the modified cladding region involves three steps, (a) stripping off the jacket (b) removal of the passive cladding, and (c) application of active cladding. In the present investigation we have used a plastic multimode fiber with core/cladding/jacket dimension of 960/40/250 µm. A meter length of optical fiber was used and a small section (1cm-4cm) of the jacket was stripped off at the center of the optical fiber. Then it is integrated with a light source and a detector. The light was focused onto the
one end of the fiber and at the other end the light intensity of the fiber was measured as shown in Fig. 6.3. The sensing probe was prepared by removing the cladding of a small portion of the fiber by polishing with the abrasive paper and application of the acetone and water on the fiber and polishing with the tissue, as explained by merchant et al. [31]. We were continuously monitoring the intensity at the other end of the fiber. We observed sudden fall in intensity at the detector end when the cladding was removed (Fig. 6.4). The SEM images of the optical fiber sensor with cladding and without cladding (sensing probe) are shown in Fig 6.5 (a) and Fig. 6.5 (b).

Fig. 6.2. Schematic diagram of the experimental set up L: Light emitting diode, F: optical fiber, C: airtight chamber, V: ammonia vapor, D: photodetector, S: signal processor.
6.3.5. Coating of Polyaniline film on optical fiber

The in-situ deposition of the chemically active polyaniline on the fiber modified section was carried out by suspending the uncladed region of the
optical fiber in the reaction container, consisting of monomer, oxidant and the dopant acid. The plastic optical fiber with core/cladding/jacket dimension of 960/40/250 µm was used in this work. The fiber with removed cladding (1-4 cm) is suspended in the reaction container, containing the aniline, ammonium peroxidisulphate and dopant acid with the optimized process parameters discussed in chapter 3 and chapter 4. Then the resulting coated fiber was removed from the solution, washed with distilled water and dried. Fig.6.5 (c) shows the SEM micrograph of the optical fiber sensor coated with PANI film by in situ chemical deposition method.

### 6.3.6. Determination of sensing properties of optical fiber sensor

An experimental set-up used for the characterization of optical fiber sensor is shown in Fig.6.2. It was designed by integrating the optical fiber sensing part with a light source, a photo detector and other electronic devices. A part of the testing fiber coated with PANI layer was placed in an indigenously developed gas sensing chamber which ensures the contact of the fiber sensing system with vapors. The sensing elements prepared were cleaved at both ends to have mirror flat edges. The cleaved sensor element is then integrated with a LED (wavelength 633 nm) light source and a silicon photo-detector (Optical Fiber test bench, Ruby Optosystems, Pune, India). The light source was focused onto the one end of the modified optical fiber sensor. At the other end, a photo detector was positioned to receive the optical signal, and convert the same to an equivalent electrical signal. The change in output power is measured when the
sensor is exposed to different concentrations of ammonia vapors (20-200 ppm) at room temperature. The sensing study of the sensor was carried out at the room temperature because the plastic optical fiber is sensitive to the temperature, and it may introduce the losses like bending, stress etc.

The influence of the sensing length on the sensor response was investigated. The sensor with different sensing length (1-4cm) was used and the response of the sensor was investigated. The effect of the source wavelength was studied, in which sources with different wavelength 450nm; 550nm and 650nm were used to test the influence of the wavelength on the sensitivity of the sensor. The effect of power variations of the source on the sensor response was investigated by varying the power of the source (1 µw - 3.5 µw).

Fig. 6.5 (a)
Fig. 6.5 SEM pictures of the optical fiber sensor a) optical fiber with cladding b) Uncladed optical fiber c) optical fiber coated with polyaniline film.
6.4. Results and Discussion

The application of polyaniline as a thin layer of a new modified cladding on an optical fiber requires the identification of both optical property and the structural quality of the polymer thin film. Thus, it is important to develop the coating methodology and also characterize the optical properties of the polymer thin film.

PANI film in presence of HCl was synthesized as per the procedure illustrated in the experimental section. The synthesized films were subjected to various characterization techniques.

6.4.1. UV-Visible characterization of synthesized PANI film on PMMA Substrate

The UV-Visible absorption spectrum of the synthesized PANI film doped with HCl is shown in Fig.6.6. The spectra show the presence of three peaks at 300, 420 and 800 nm together with a shoulder at 600 nm in DMSO (dimethyl sulfoxide) as a solvent. The peak at 300 nm corresponds to the $\pi-\pi^*$ transition of the benzenoid rings, while the peak at 400 nm can be assigned to the localized polarons that are characteristic of the protonated polyaniline, together with an extended tail at 800 nm representing the conducting emeraldine salt phase of the polymer. The shoulder at 600 nm represents the insulating pernigraniline phase of the polymer. This reflects that the polymer is composed of different mixed phase [32].
Fig. 6.6 UV-Visible spectrum of synthesized PANI-HCl film.

Fig. 6.7 FTIR spectrum of synthesized PANI-HCl film.
6.4.2. FTIR Analysis of synthesized PANI film on PMMA Substrate

The molecular structure of synthesized PANI-HCl film was studied using FTIR spectroscopy. The FTIR spectrum of synthesized PANI-HCl film is shown in Fig.6.7. It can be seen that quinoid and benzenoid ring stretching bands are present at 1561 cm\(^{-1}\) and 1480 cm\(^{-1}\). The C-H in plane and C-H out of plane bending vibrations appears at 1106 cm\(^{-1}\) and 704 cm\(^{-1}\). The peak at 1295 cm\(^{-1}\) is assigned to C-N stretching of secondary aromatic amine. Band at 3440 cm\(^{-1}\) is assigned to the N-H stretching band. All these characteristic bands confirm the presence of conducting ES phase of the polymer. This shows very good agreement with earlier reported work [32-34].

6.4.3. Surface Morphology of synthesized PANI film on PMMA Substrate

The surface morphology of the synthesized PANI-HCl film was studied by using scanning electron microscope (SEM). The scanning electron micrograph of the synthesized PANI film is shown in Fig 6.9. We observed granular and porous surface morphology with very good uniformity which is suitable for sensor applications.

6.4.4. I-V characteristics of synthesized PANI film on PMMA Substrate

The current-voltage (I-V) characteristics of the synthesized PANI films were studied to ensure an ohmic behavior of the films. A linear relationship of the I-V characteristics shown in Fig.6.8 reveals that the polyaniline film has an ohmic behavior.
Fig. 6.8 I-V characteristic of synthesized PANI-HCl film.

Fig. 6.9 The scanning electron micrograph of synthesized PANI-HCl film.
6.4.5. Sensing behavior of synthesized PANI film on PMMA Substrate

In order to evaluate the ammonia gas-sensing characteristics of the synthesized PANI-HCl film at room temperature, we have used the Four-probe technique of resistivity measurement, where four electrical contacts were made on the polyaniline film. The polyaniline film was kept in indigenously designed and fabricated a gas chamber. The synthesized PANI-HCl film was exposed to ammonia gas for 6 minutes. The recovery time was measured by exposing the film to the air for 6 minutes. The change in resistivity of the film was measured at an interval of 15 s. We have explored the ammonia gas-sensing curves of PANI-HCl film at three different concentrations of gas, 20 ppm, 100 ppm, and 250 ppm. It was observed that the resistivity of the polyaniline film increases in the presence of ammonia and after a few minutes becomes saturated and the resistivity decreases steadily to a minimum value, when the ammonia gas was removed however, a small drift from its original value was observed. The relationship between change in resistivity and time of the synthesized PANI-HCl film when exposed to different concentration of ammonia gas are shown in Fig. 6.10. The conductivities of PANI were decreased by exposure to NH$_3$ vapors. The changes in conductivity of polymers are attributed to the consumption of charges from the polymeric backbone [35]. The sensing mechanism is explained by the compensation effect [36]. When the conductive emeraldine salt is exposed to NH$_3$ gas, the dopant is partially reduced, which leads to a decrease of electrical conductivity [37]. Extensive studies of the gas-sensing properties of conducting polymers show that when these polymers are exposed to electron-
donating gases such as ammonia, if the gases are absorbed, the polymers exhibit an increase in resistance [38], while an increase in conductivity is observed with gases such as HCl [39, 40].

The polyaniline film was enclosed in indigenously designed and fabricated a gas chamber. The synthesized PANI film was exposed to ammonia gas for 6 minutes. The recovery time was measured by exposing the film to the air for 6 minutes. The change in resistivity of the film was measured at an interval of 15 s. The film shows response to the ammonia vapor. We have explored the ammonia gas-sensing curves of PANI at three different concentrations of ammonia.

![Graph showing response of synthesized PANI film to ammonia gas](image)

**Fig.6.10** Response of the synthesized PANI film to ammonia gas (a) 20 ppm (b) 100 ppm (c) 250 ppm.

We have studied the sensing behavior of PANI-HCl optical fiber sensor. Fig. 6.11 shows the response curve of the sensor when exposed to ammonia. For the purpose of investigation of reproducibility and response characteristics of the sensor three measurements were continuously carried out. PANI-HCl optical fiber sensor (with 2 cm sensing probe length) was exposed to 50 ppm of ammonia vapor and change in output power was observed. We observed excellent repeatability. This is one of the important characteristics of the sensor. We observed very good response time (10 min) and recovery time (10 min).

![Graph showing the response curve of the sensing system to 50 ppm of ammonia.](image)

Fig. 6.11 The response curve of the sensing system to 50 ppm of ammonia.
Fig. 6.12 The response of the optical fiber sensor to different ammonia concentration.

Fig. 6.12 shows the response of the PANI-HCl optical fiber sensor for different concentration of ammonia vapor. The length of sensing probe was 2 cm. It shows linear response for 50 ppm to 200 ppm of ammonia concentration.

**6.4.7. Effect of the sensing length of the sensing probe**

The different sensing probes i.e. 1 cm to 4 cm were prepared and coated with polyaniline film doped with HCl with the optimized parameters. Fig. 6.13 shows the sensor response for various sensing probes. We observed best response for 2 cm length of sensing probe, when it was exposed to 50 ppm of ammonia vapor. The decrease in output power (intensity) with increasing sensing length is attributed to the increase in the number of leaky modes. The increase in the sensor response is due to the increase in sensing probe length from 1 cm to 2 cm, however for 3 cm and 4 cm we observed very low sensor response.
response, which may be due to the fact that, more sensing length incorporates more leaky modes and hence less light will interact with the film and therefore the sensor response is significantly low.

![Graph showing sensor response for different sensing length](image)

**Fig. 6.13 Sensor response for different sensing length**
A: 4 cm; B: 3 cm; C: 1 cm; D: 2 cm.

### 6.4.8. Influence of the wavelength of light on sensing response of the sensor

The light sources with wavelength 450nm, 550nm and 650nm were used to study the influence of the light wavelength on the sensing response of the sensor. The sensing probe of 2 cm length was used and it was exposed to 200 ppm of ammonia vapor. The change in output power (intensity) for various wavelengths was recorded (Fig. 6.14). We observed excellent response i.e. change in power (intensity) for 650 nm wavelength as compared to 550 nm and 450 nm.
of wavelength. This indicates that the sensor response is highly dependent on the source wavelength.

Fig. 6.14 Response of the sensor with variation in source wavelength.

Fig. 6.15 Response of the sensor for different source power. A: 1µw; B: 2µw; C: 3µw; D: 3.5µw.
6.4.9. Effect of the source power on the sensing response of the sensor

The influence of light intensity of source on sensor response (when it is exposed ammonia vapor) has also been investigated using Optical Fiber test bench, Ruby Optosystems, Pune, India. The sensor response was observed for 1µw, 2 µw, 3 µw, 3.5 µw of source power (Fig.6. 15). The change in output power was maximum for 3.5 µw source power. This may be due to fact the more source power has the more evanescent power available at the sensing region, which incorporates more interaction with the film.

6.5. Conclusion

We have designed and developed PANI-HCl optical fiber based chemical sensor for ammonia gas sensing. The sensor is based on modified cladding approach. i.e. ammonia sensitive layer was deposited on the sensing region of the sensor. A simple approach was used to design this sensor. Initially, an optimization of various parameters viz. concentration of monomer, oxidants, doping acids, deposition time and reaction temperature was carried out on the PMMA substrate, for the synthesis of PANI-HCl film. Its sensing response to ammonia was also studied. Then the PANI-HCl film with optimized parameters was deposited on sensing probe of optical fiber and its sensing response was studied. It shows excellent sensing response with response time (10 min) and recovery time (10 min) for 20 ppm of ammonia with 2 cm length of sensing probe,650 nm of source wavelength and 3.5 µw of source power.
References:


