Development of PANI-AA Optical Fiber Ammonia Sensor

7.1. Introduction

This chapter is focused on the development, characterization and optimization PANI-AA optical fiber ammonia sensor. The foundation of the 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 modified cladding technique, i.e. the ammonia sensitive material; the conducting polymer film of the polyaniline doped with (Acrylic acid) AA, sensitive to ammonia gas with optimized synthesis parameters was coated on a small section of the uncladed fiber. This polyaniline coated optical fiber sensor exhibit excellent response to ammonia vapor at room temperature. The sensor has been developed by applying a coating of polymer material, polyaniline doped with AA on uncladed region of the fiber using in-situ chemical polymerization, which provides the optimal 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 SnO₂ and Fe₂O₃ 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 light 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 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 construction 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 fiber ammonia gas sensor, which is sensitive, easy to regenerate and inexpensive.

7.2. Theoretical part

The designing aspect of fiber optic sensor is already been discussed in Chapter 5.

7.3. Experimental

7.3.1. 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), Acrylic acid and HCl was purchased from Loba Chemie (India). Aniline was doubly distilled before use.

7.3.2. Instrumentation:

This part has already been discussed in chapter 5.

7.3.3. Synthesis of PAN-AA film by chemical polymerization on PMMA substrate

Aniline monomer and AA were purified by distillation prior to use. All other reagents were of analytical grade and were used as received. PANI-AA was synthesized using in-situ polymerization of aniline monomer by using ammonium peroxydisulfate (APS) as an oxidant in the presence of AA 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, 0.50 M of AA 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 AA 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.

7.3.4. Preparation of optical fiber sensing element

Preparation of the sensing element is already been discussed in Chapter 5.

7.3.5. Coating of PANI–AA film on optical fiber

The in-situ deposition of the chemically active PANI–AA on the fiber modified section was carried out by suspending the uncladded 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. 7.1 (a)-(c) shows the SEM micrographs of the optical fiber sensor.

7.3.6. Determination of sensing properties of optical fiber sensor

An experimental set-up used for the characterization of optical fiber sensor as shown in earlier chapter. 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 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 was measured when the sensor was 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).

7.4. 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 films in presence of AA were synthesized as per the procedure illustrated in the experimental section. The synthesized films were subjected to various characterization techniques.

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

The UV-Visible absorption spectrum of the synthesized PANI-AA film with optimized concentration of aniline, AA and APS is shown in Fig.7.2. The peak at 320 nm corresponds to the \( \pi-\pi^* \) transition of the benzenoid rings, while the sharp groove at 440 nm can be assigned to the localized polarons which are characteristic of the protonated polyaniline, together with the extended tail at 800
nm representing the conducting emeraldine salt (ES) form of the polymer film [32].
Fig. 7.1 (c)

Fig. 7.1 SEM pictures of the optical fiber sensor a) optical fiber with cladding b) Uncladded optical fiber c) optical fiber coated with polyaniline film.

Fig. 7.2 UV-Visible spectrum of synthesized PANI-AA film.
7.4.2. FTIR Analysis of synthesized PANI-AA film on PMMA substrate

The molecular structure of synthesized PANI-AA films was studied using FTIR spectroscopy. The FTIR spectrum of synthesized PANI-AA film with optimized concentration of aniline, AA and APS is shown in Fig. 7.3. It can be seen that quinoid and benzenoid ring stretching bands are present at 1577 cm\(^{-1}\) and 1490 cm\(^{-1}\). The C-H out of plane bending vibrations appears at 750 cm\(^{-1}\) and the band of C-H stretching vibration in the plane of 1, 1-substituted benzenoid ring at 815 cm\(^{-1}\) can be seen. The peak at 1287 cm\(^{-1}\) is assigned to C-N stretching of secondary aromatic amine. In addition, a relative weak peak at 1735 cm\(^{-1}\) appears in the spectrum is due to the stretching vibration of carbonyl group and it shows presence of AA in the film. Band at 3400 cm\(^{-1}\) is assigned to the N-H stretching band. All these characteristic bands confirm the presence of conducting polyaniline (PANI). This shows very good agreement with earlier reported work [32-34].
7.4.3. Surface Morphology of synthesized PANI–AA film on PMMA substrate

The surface morphology of the synthesized PANI–AA film was studied by using scanning electron microscope (SEM). The scanning electron micrograph of the synthesized PANI film is shown in Fig. 7.4. We observed granular and porous surface morphology with very good uniformity which is suitable for sensor applications.

7.4.4. I-V characteristics of synthesized PANI–AA film on PMMA substrate

The current–voltage (I-V) characteristics of the synthesized PANI–AA film was studied to ensure an ohmic behavior of the films. A linear relationship of the I-V characteristics shown in Fig. 7.5 reveals that the polyaniline film has an ohmic behavior.

![Fig7.4 The scanning electron micrograph of Synthesized PANI-AA film](image-url)
7.4.5 Sensing behavior of synthesized PANI-AA film on PMMA substrate

Sensing behavior of the synthesized PANI film was studied using indigenously developed computer controlled gas sensing chamber. The synthesized PANI film was exposed to ammonia gas for 7 minutes. The recovery time was measured by exposing the film to the air for 7 minutes. The change in resistance of the film was recorded at an interval of 15 second. It is reported that anything above 120 ppm of ammonia in the environment is hazardous and dangerous to health of the human being. Therefore, we have tested synthesized PANI-AA films for 20, 100 and 250 ppm of ammonia. The relationship between change in resistivity of the synthesized PANI film with time when exposed to 20 ppm, 100 ppm and 250 ppm concentration of ammonia gas is shown in Fig.7.6. It was observed that the resistance of the polyaniline film increases when exposed to ammonia; it reaches a maximum value and becomes
The resistance decreases steadily to a minimum value, when the ammonia gas was removed; however, a drift from its original value was observed. The response time for the film was found to be 180 s and the recovery time is found to be 300 s.

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

**Fig. 7.6** 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-AA optical fiber sensor. Fig. 7.7 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. The PANI-AA optical fiber sensor (with 2 cm sensing probe length) was exposed to 20 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 (9 min) and recovery time (9 min).

Fig. 7.8 shows the response of the PANI-AA 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.

Fig. 7.9 shows the response curve of the PANI-AA optical fiber sensor as a function of time for different concentration of ammonia (50 ppm-250 ppm). The 2 cm sensor was used for the sensor response. The sensor shows the change in output power with the increase in gas concentration from 50 ppm to 250 ppm.

7.4.7. 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 acrylic acid with the optimized parameters. Fig. 7.10 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, which may be due to the fact that more sensing length incorporates more leaky modes and hence less light can interact with the film and therefore the sensor response is significantly low.
Fig. 7.7 The response curve of the sensing system to 20 ppm of ammonia.

Fig. 7.8 The response of the optical fiber sensor to different ammonia concentration.
Fig. 7.9 The response of the sensor when exposed to different Concentration ammonia gas (50-250 ppm) and open to air.

Fig. 7.10 Sensor response for different sensing length
A: 4 cm; B: 3 cm; C: 1 cm; D: 2 cm.
7.4.8. 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.7.11). 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.

7.4.9. Effect of the source power on 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.

![Graph showing change in output power with time for 450 nm, 550 nm, and 650 nm wavelengths](Image)

Fig.7.11 Response of the sensor with variation in source wavelength.
The sensor response was observed for 1 µw, 2 µw, 3 µw, 3.5 µw of source power (Fig. 7.12). 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.

7.5. Conclusions

We have designed and developed PANI-AA 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-AA film. Its sensing response to ammonia was also studied. Then the PANI-AA 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 (9 min) and recovery time (9 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:


