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A novel low cost plastic optical fiber chemical sensor using polyaniline film

K. P. KAKDE, H. J. KHARAT, P. A. SAVALE, K. DATTA, P. GHOSH, D. SHIRSAT*
Optoelectronics and Sensor Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431 004, Maharashtra, India

We have developed a fiber-optic chemical sensor by replacing a certain portion of the original cladding by a chemically sensitive material, specifically, polyaniline. 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; 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. Coating technique i.e. in-situ chemical polymerization was used. 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.

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Keywords: Fiber-optic chemical sensor, Modified cladding, Conducting polymer, Sensor technology

1. Introduction

In recent years, a lot of attention has been given to the use of conducting polymers in chemical sensors, as sensing layers for gases detection, because of merits such that easy fabrication, low power consumption, and 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_2O_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 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 paper, 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. The ammonia sensitive film of the conducting polymer (PANI) doped with Acrylic acid (AA) as a novel material, has been optimized on PMMA substrate. The parameters like conductivity, adhesitivity to substrate, porosity, uniformity and sensitivity to ammonia gas of the film have been optimized on the PMMA substrate, since the similar material i.e. PMMA has been used in the optical fiber. Therefore it becomes quite easy to carry out the optimization of the above parameters on the PMMA substrate than 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. Then the film with optimized parameters was deposited on the optical fiber. The optical properties of the sensor have been studied by indigenously developed gas sensing chamber and fiber optic bench, when the sensor is exposed to the ammonia vapor. We have studied electrical and optical responses of the sensor using independent

experimental setup. 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 critical components are required, in general, for constructing a fiber-optic sensor: 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 method is illuminated with the light emitting diode (LED). The conducting polymer is uniformly deposited onto core 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 the 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.

2. Theoretical part

The configuration of the fiber-optic sensor is created on the fiber itself, as shown in Fig. 1, using the cladding modification methodology. In a small section of an optical fiber, the original passive cladding is replaced by a sensitive 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. The partial leaky-mode sensor has been constructed 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 from the ray theory 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. 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. 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

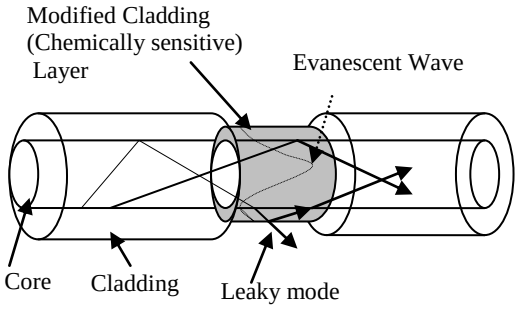

Fig. 1. Structure of modified cladding fiber optic chemical sensor.

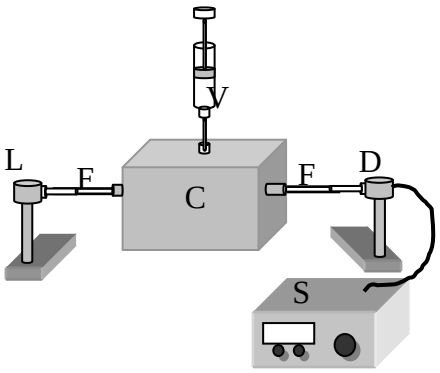

Fig. 2. Schematic diagram of the experimental set up L: Light emitting diode, F: optical fiber, C: airtight chamber, V: ammonia vapor, D: photodetector, S: signal processor.

3. Experimental

3.1 Synthesis of polyaniline film by chemical polymerization

Aniline monomer and AA were purified by distillation prior to use. All other reagents were 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.

3.2 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. A plastic multimode fiber with core/cladding/jacket dimension of 960/40/250 µm was used in this work. A meter length of optical fiber is used and a small section (1 cm-4 cm) of the jacket was stripped off the center of the optical fiber,the SEM micrograph of the optical fibeer with jacket stripped off is shown in Fig. 4. 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. 3. The sensor 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],The SEM in Fig. 5 shows the uncladed fiber. While doing this the intensity at the other end of the fiber was continuously monitored and we observed a sudden fall in intensity when the cladding of the fiber was removed, which confirms that only the cladding was removed from the fiber. The in-situ deposition of the chemically active polyaniline on the fiber modified section is achieved 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 the acrylic acid with the optimized reaction and the process parameters discussed earlier in section (3.1). The resulting coated fiber was removed from the solution, washed with distilled water and dried. The SEM picture of the optical fiber sensor coated with PANI film by in situ chemical deposition method is shown in Fig. 6.

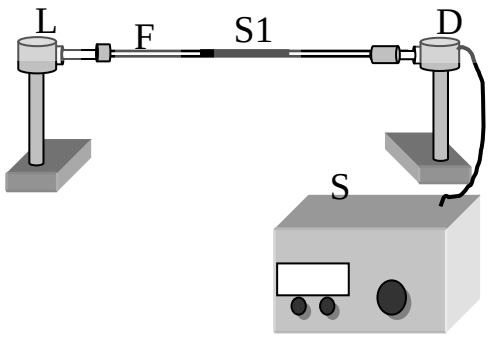

Fig. 3. Schematic diagram of the experimental set up for removal of cladding. L: Light emitting diode, F: optical Fiber, D: photodetector, S: signal processor. S1: sensing element.

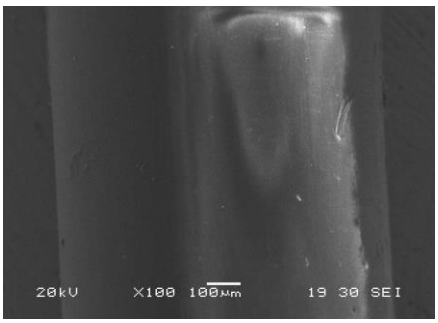

Fig. 4. SEM picture of the optical fiber with cladding.

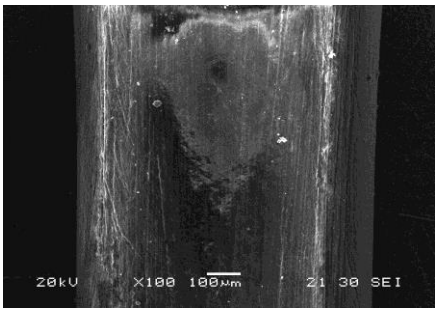

Fig. 5. SEM picture of the uncladed optical fiber.

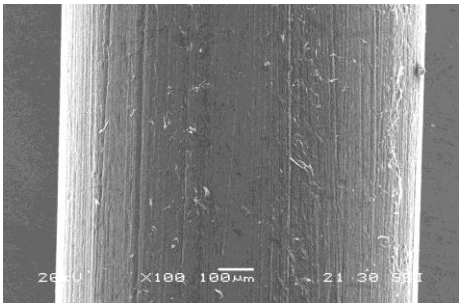

Fig. 6. SEM picture of optical fiber coated with polyaniline film.

3.4. Determination of sensing properties of optical fiber sensor

An experimental set-up used for the characterization of optical fiber sensor is shown in Figure2. 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 similarly to avoid stress – induced bending effects, the optical sensing was done using small optical fiber of 1 meter length by keeping the fiber unbend.

The influence of the sensing length on the sensor response was investigated. The sensor with different sensing length (1-4 cm) was used and the response of the sensor was investigated. The effect of the source wavelength was studied, in which sources with different wavelength 450 nm, 550 nm and 650 nm 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).

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.

4.1. UV-Visible characterization of synthesized PANI films

The UV-Visible absorption spectrum of the synthesized PANI films doped with AA is shown in Fig. 7. The peak at 320 nm corresponds to the π-π* transition of the benzenoid rings, while the sharp trough 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 ES form of the polymer film [32].

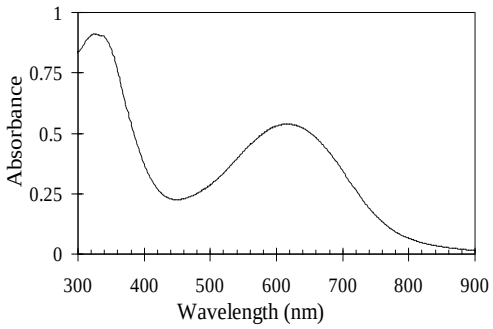

Fig. 7. UV-Visible spectrum of synthesized PANI film.

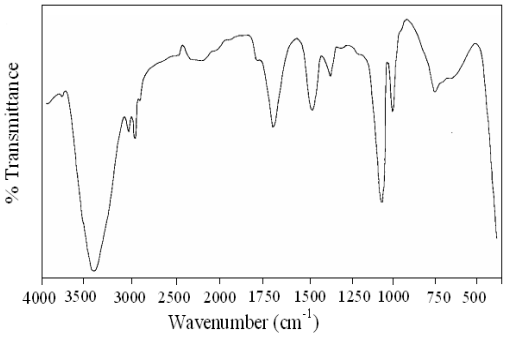

Fig. 8. FTIR spectrum of synthesized PANI film.

4.2. FTIR Analysis of synthesized PANI films

The molecular structure of synthesized PANI films was studied using FTIR spectroscopy. The FTIR spectrum of synthesized PANI film is shown in Fig. 8. It can be seen that quinoid and benzenoid ring stretching bands are present at 1653 cm^{-1} and 1423 cm^{-1}. The C-H in plane and C-H out of plane bending vibrations appears at 1024 cm^{-1} and 952 cm^{-1}. The peak at 1315 cm^{-1} is assigned to C–N stretching of secondary aromatic amine. In addition, a relative weak peak at 1700 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 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].

4.3. Surface Morphology of synthesized PANI film

The surface morphology of the synthesized PANI films was studied by using scanning electron microscope (SEM).The scanning electron micrograph of the synthesized PANI film is shown in Fig. 9. We observed granular and porous surface morphology with very good uniformity which is suitable for sensor applications.

4.4. I-V characteristics of synthesized PANI films

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. 10 reveals that the polyaniline film has an ohmic behavior.

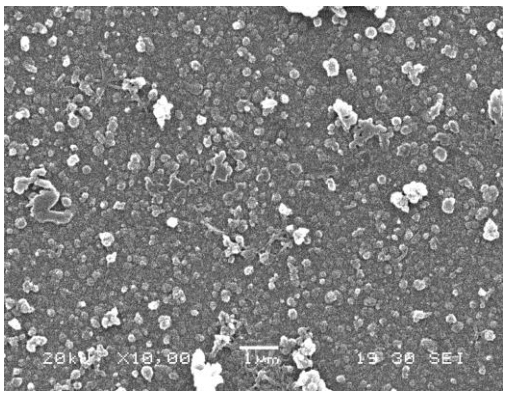

Fig. 9. The scanning electron micrograph of film synthesized PANI film.

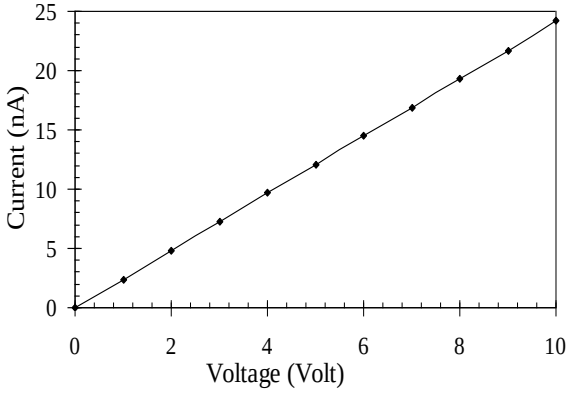

Fig. 10. I-V characteristic of synthesized PANI film.

4.5. Sensing behavior of synthesized PANI films

Sensing behavior of the synthesized PANI films was studied using indigenously developed computer controlled gas sensing chamber. The synthesized PANI films were 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 seconds. It is reported that any thing 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. 11. It was observed that the resistance of the polyaniline film increases when exposed to ammonia; it reaches a maximum value and becomes constant. 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.

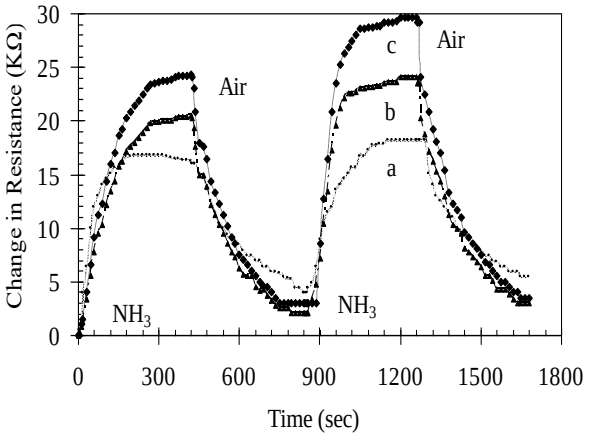

Fig. 11. Sensing behaviour of PANI film for concentrations of ammonia (a)20 (b)100 (c) 250 ppm .

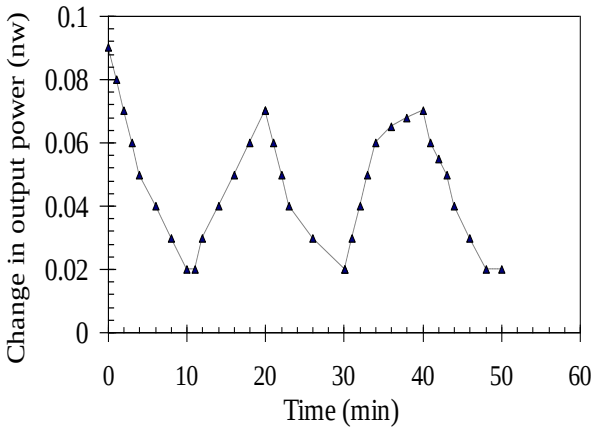

Fig. 12. The response curve of the optical fiber sensosr to 20 ppm of ammonia gas.

4.6. Effect of the ammonia vapor on the output intensity of the sensor

Fig. 12 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 was continuously carried out. The 2 cm sensor was exposed to 20 ppm of ammonia vapor and change in output power of the sensor was observed. All of the measurements are almost same. This is the one of the important characteristics of the sensor. In addition to this the sensor has recovery time below 10 min. The sensor has fast recovery time and good repeatability.

Fig. 14 shows the response of the sensor for different concentration of ammonia vapor. The length of sensor was 2 cm. It shows linear response for 50 ppm to 200 ppm of ammonia concentration.

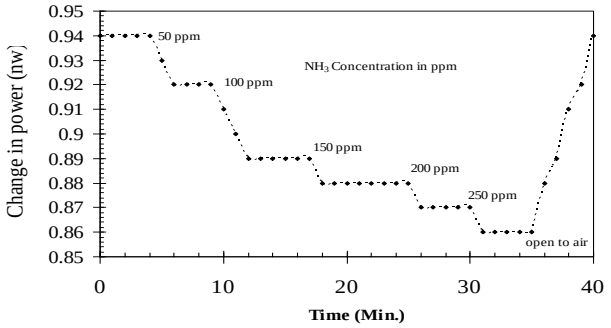

Fig. 13. The response of the optical fiber sensor to different ammonia concentration.

Fig. 13 shows the response curve of the 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. The sensor response time is 5 minutes. It also showed very fast recovery (i.e. 5 minutes).

4.7. Effect of the sensing length of the sensor

The different sensing elements i.e. 1 cm to 4 cm were prepared and coated with polyaniline film doped with acrylic acid with the optimized parameters. Fig. 15 shows the sensor response for four sensing elements. We observed best response for 2 cm sensing element, 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 sensor length from 1 cm to 2 cm, but for 3 cm and 4 cm sensor response is less i.e. the change in power (intensity) is less, which may be due to the more sensing length which incorporates more leaky modes and hence less light can interact with the film and therefore the sensor response is less.

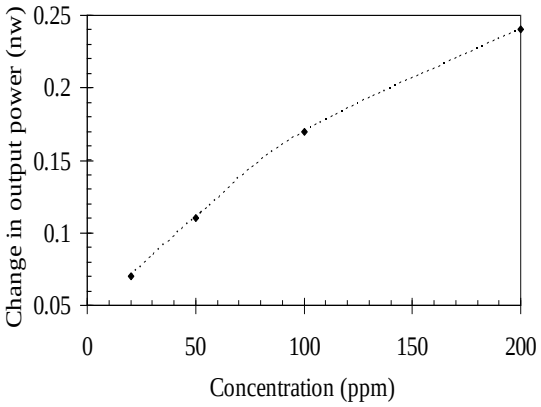

Fig. 14. The response of the sensor when exposed to different concentration of ammonia gas (50-200 ppm).

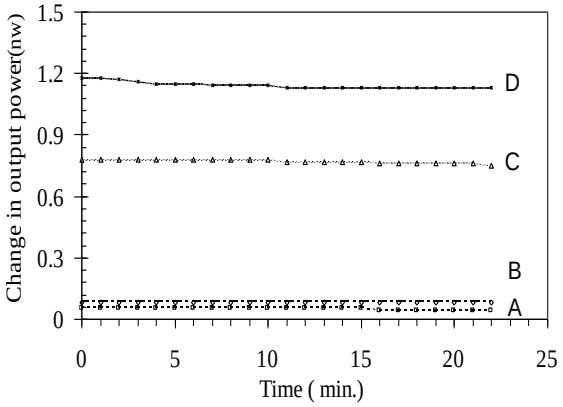

Fig. 15. Sensor response for different sensing length A: 4 cm;B: 3 Cm; C: 1 cm; D: 2cm.

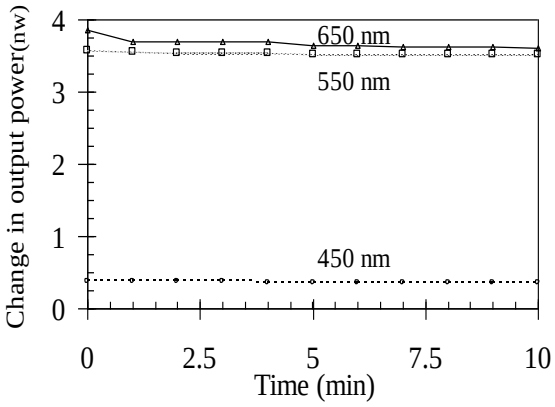

Fig. 16. Response of the sensor with variation in source wavelength.

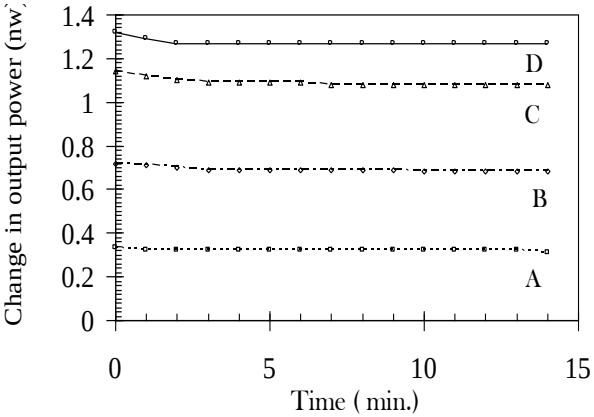

Fig. 17.Response of the sensor for different source power. A: 1µw; B: 2 µw; C: 3 µw; D: 3.5 µw.

4.8. Influence of the wavelength of light on fiber-optic sensors

The light sources with wavelength 450 nm, 550 nm and 650 nm were used to study the influence of the light wavelength on the sensitivity of the sensor. The 2 cm

sensor coated with sensing film was used and the sensor was exposed to 200 ppm of ammonia vapor. The change in output power (intensity) for these wavelengths is shown in Fig. 16. We observed excellent response i.e. change in power (intensity) for 650 nm wavelength as compared to 550 nm and 450 nm of wavelength. Thus the sensor response is highly dependent on the source wavelength

4.9. Effect of the source power

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 obtained for 1 µw, 2 µw, 3 µw, 3.5 µw as shown in Fig. 17. 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 sensor, which incorporates more interaction with the film.

This sensor has good sensitivity to ammonia which is due to the optimization of the optical system i.e. source wavelength, power of the source and the optimization of the synthesized PANI film parameters. This sensor gives excellent response to ammonia at 650 nm source wave length because Polyaniline has good absorption at 650 nm wavelength of light when it is exposed to ammonia. The selectivity issue of the sensor is being pursued.

5. Conclusions

We have designed and developed an 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 core of the sensor. A simple approach was used to design the sensor. An optimization of the ammonia sensitive layer was carried out on the PMMA substrate first, which has advantages to carry out different characterizations easily. A sensitive, simple and low-cost fiber-optic sensor was successfully designed and developed. The sensing properties of the optical fiber sensor for ammonia vapors at room temperature have been studied. We observed linear response for 20-200 ppm of ammonia. It also exhibits good reversibility and repeatability. These experimental results have demonstrated that a low cost plastic optical fiber sensor for ammonia gas can be designed and developed.

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*Corresponding author: mdshirsat_bamu@yahoo.co.in; mds_bamu@yahoo.co.in