Chapter 5

FIBER OPTIC EVANESCENT WAVE SENSORS FOR AMMONIA GAS SENSING

This chapter describes the design, development and characterization of two different types of fiber optic sensors viz. unclad evanescent wave fiber optic sensor (EWFS) and long period grating (LPG) EWFS for the detection of toxic ammonia gas. Sol-gel technology is used in both the cases for immobilizing a reversible ammonia sensitive dye on the unclad or LPG region of the fiber. Ammonia gas permeating into the immobilized dye converts the color of the dye reversibly from yellow to blue with increasing concentration of ammonia gas. The concentration of ammonia gas can be determined by measuring the absorption at a given wavelength. The response time, recovery time, reusability etc of the developed sensors are also illustrated. The techniques described here are also relevant to the detection of a wide range of other gases.
5.1. Introduction

Ammonia plays an important role in atmospheric chemistry and gives rise to serious environmental problems. The excess presence of ammonia in the atmosphere causes direct and indirect damage to human being and to the ecosystems, the indirect effect being more serious and widespread than the direct effect [1]. Due to an increasing environmental awareness and stricter regulations for pollution control, on-line monitoring of ammonia gas has got wide-spread interest. Moreover, in industry, continuous ammonia measurement is desired in food and clinical analysis.

On-line determination of ammonia in gaseous or liquid state is often accomplished by potentiometric electrodes [2-4]. But this type of sensors have the disadvantages like (a) they do not lend themselves to miniaturization: (b) they are not easy to sterilize: (c) short life time: (d) their performance can be affected by surface potentials and results in signal drift: and (e) they require reference electrodes. Other class of ammonia sensing device is commercial infrared gas analyzers. The infrared devices, although quite sensitive, are nevertheless expensive and bulky.

Spectrophotometric methods of sensing chemical species are not a new technique. Spectrophotometers are used for the recognition of a wide range of chemical species from their characteristic absorption, florescence or Raman spectra. Optical gas sensing methods are essentially similar, but usually are more dedicated versions of such spectrophotometers. All are based on the irreversible change in color occurring as a result of a chemical reaction. These methods are suitable for the determination of total ammonia concentration, but frequently require separation of the analyte from the sample or masking of possible interferents. This makes the procedures time-consuming and complicated. Typical examples are the well known indophenol method, Nessler’s method or the Berthelot reaction [5,6].

Most of these problems can be solved by using optical methods, ideally in combination with fiber optics. Most of the fiber optic gas sensors are based on simple absorption; although sensors based on Raman scattering mechanism or florescence
effect have been reported. The first description of an organic film-coated optical waveguide sensor for vapor detection was published by Hardy et al. [7] in 1975. A picrate dye was used as the selective chemical indicator for cyanide vapors. Subsequently, David et al. [8] and Orofino et al. [9] described a similar device incorporating a ninhydrine-coated quartz rod that could detect ammonia vapor concentrations below 100 ppb. For both of these devices, however, the dye reactions are chemically irreversible and hence are of limited practical use. In 1983, Guiliani et al. [10] reported a reversible sensor for ammonia gas consisting of a 90mm long commercial soda-glass capillary tube coated with an oxazine perchlorate dye. However, the lowest detectable ammonia concentration reported was about 10ppm. After that, Beyler et al. reported a fiber optic sensor employing immobilization of ammonia sensitive dye on the fiber surface [11]. Nevertheless, this method appeared to have problems in achieving the necessary reversibility.

Porous glass optical fiber with an associated dye has also been used as a sensor for the detection of ammonia vapors at low concentrations [12]. The porous structure that remains after selective heat treatment, phase separation and chemical leaching of a borosilicate glass imparts a high surface area to the fiber core. Ammonia vapors permeating into the porous zone, which is pretreated with a reversible pH dye indicator, produce a spectral change in transmission. The resulting pH change is measured by in-line optical absorbance and is proportional to the ambient-ammonia concentration. Possible problems that could occur with this method include surface absorption, contamination etc.

A porous cellulose tape impregnated with a processing solution which changes color with ammonia gas has been used for ammonia gas sensing [13-15]. Nobuo Nakano et al. reported tape monitor based on the change in fluorescence intensity of a pH indicator (Eosine) put on the tape for the detection of ammonia gas in air [16]. Exposure of ammonia gas to the tape increases the pH of a solution existing in the tape. The resultant compound produced with ammonia gas shows an excitation maximum at 460nm and fluorescence maximum at 550nm. The degree of
the change in fluorescence intensity is proportional to the concentration of ammonia

gas at a constant sampling time and flow rate. However, the sensitivity and precision

of these methods should be significantly improved when measurements are made

without removing the tape from the sampling chamber.

Another method for ammonia gas sensing is by using conducting polymers. They 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. Conducting polymer gas sensors commonly rely on conductivity changes that occur when they are exposed to certain gases. The dc conductivity of a polypyrrole film decreases with increasing ammonia gas concentration and an ammonia gas sensor based on this property has been reported [17]. Similarly, the dc conductivity of polyaniline also depends on ammonia gas concentration. A polyaniline film containing nickel prepared by electrochemical oxidation could detect ammonia gas in the range 1-10000 ppm at room temperature [18,19,20]. However, the response time of these sensors depends on temperature and heating is required to regenerate the sensor.

Within the last decade, sol-gel route opened up new possibilities for the fabrication of fiber optic sensors for different gases [21-30] and a wide variety of metal ions in solutions [31,32]. The sol-gel process is a liquid-phase method of preparing glasses and ceramics at ambient temperatures, by the hydrolysis and polymerisation of organic precursors followed by room temperature curing. Klein et al. reported a fibre optic evanescent wave integrated ammonia sensor using this technology [33]. The sensitive element of that sensor is a strip waveguide, fabricated by field-assisted ion exchange, coated with an immobilised indicator dye. However, the sensitivity of the sensor can be further improved by using optical fiber itself as the sensing element instead of glass slide and when multiple sol-gel coating are used at the sensing region instead of single coating [34] for immobilisation of the dye.
In the coming sections, we discuss two novel fiber optic sensors, viz. unclad fiber optic evanescent wave sensor (EWFS) and long period grating (LPG) EWFS, for ammonia gas detection that eliminate most of the difficulties and disadvantages of the above mentioned methods. In both these sensors, a part of the optical fibre itself is employed for making the sensing region and multilayer sol-gel coating is provided at the sensing region for immobilizing the ammonia sensitive dye, bromcresole purple, by dip coating method.

5.2. Sol-gel technology

The sol-gel process is a well-known method for chemical synthesis and for the preparation of numerous ceramic and glassy materials. This method typically involves the hydrolysis and condensation of metal alkoxide precursors to form gels which are later densified at much lower temperatures than are required by conventional ceramic processing techniques [35]. The versatility of this process is evidenced from the silicate based systems, which have been developed into a wide variety of final products ranging from catalytic supports [36] and photochromic glasses [37] to planar waveguides [38] and fiber optic preforms [39]. The process can be tailored to yield materials of the desired composition and physical properties in the form of powders, fibers, thin films and monoliths [40]. One of the advantages of using sol-gel process is a high degree of purity and homogeneity due to mixing at near molecular levels. Moreover, due to the low processing temperatures, amorphous compositions, which are unstable if produced by melting, can be made by the sol-gel route.

By extending this concept to include organic compounds, which decompose at high temperatures, a completely new class of materials has emerged since the early 1980s [41-46]. These compounds can be dyes, biomolecules such as enzymes or monomers, which subsequently polymerize. The sol-gel derived xerogels doped with organic dyes have been extensively used in dye-based lasers [43], as structural probes [44] and as chemical sensors [45-46]. This type of glass can be porous, where the porosity and hence the refractive index can be controlled over a wide range by
adjusting the fabrication conditions such as temperature or pressure. The inorganic gel is chemically and photochemically stable as compared with polymers and solvents. Since the gel can be easily formed into fibers and coatings, they can be coupled with optical fibers to form miniaturized sensors for on-line monitoring.

5.2.1. Sol-gel chemistry

The main processes that involve in the sol-gel glass or ceramic production are hydrolysis and condensation of a metal alkoxide precursor (starting material). The precursor used in the present investigation is tetraethyl orthosilicate (Si(OR)₄). The hydrolysis reaction proceeds through three steps, which are described by nucleophilic substitution [47,48]. In the first stage of hydrolysis, the nucleophilic attack of the positively charged metal atom results from its interaction with negatively charged oxygen atom that is associated with a water molecule and as a result, the coordination number of the metal atom increases. Subsequently, the transfer of a positively charged proton to a negatively charged OR group of the metallo-organic precursor occur and finally, the R-OH molecule is released as the product, completing the sequence of hydrolysis reaction. Equation 5.1 represents the hydrolysis reaction of the tetraethyl orthosilicate precursor.

\[
\text{Si(OR)₄} + H₂O \rightarrow \text{HO-Si(OR)₃} + R-OH
\]  \hspace{1cm} (5.1)

The hydrolysis of a silicon alkoxide yields silanol groups (Si-OH) and ethanol. These silanols eventually undergo the condensation reaction, where, two partially hydrolysed molecules are linked together as shown in equations 5.2 and 5.3.

\[
(\text{OR})₃ \text{Si-OH} + \text{HO-Si(OR)₃} \rightarrow (\text{OR})₃ \text{Si-}
\]

\[
\text{O-Si(OR)₃} + \text{H₂O}
\]  \hspace{1cm} (5.2)

or

\[
(\text{OR})₃ \text{Si-OR + HP-Si(OR)₃} \rightarrow (\text{OR})₃ \text{Si-O-Si(OR)₃} + \text{R-OH}
\]  \hspace{1cm} (5.3)

According to equation 5.2 and 5.3, an alcohol condensation may be responsible for the polymerization of hydroxylated groups, so that condensation by this mechanism results in the bridging of an oxygen atom between two silicon atoms. Once a hydrated metal group is formed, each of the above chemical equations are possible, and
therefore a competition between the hydrolysis and polycondensation reactions continues throughout the reminder of the sol-gel process [49].

5.2.2. Sol-gel coating methods

The most important application of sol-gel processing is for coating and thin films production such as electronic films, porous coatings, protective coatings and optical coatings [40,50]. The two widely practiced methods of sol-gel deposition are dip-coating and spin coating.

5.2.2.1. Dip-coating:

Dip coating is a simple way of depositing films onto a substrate such as small

\[ h = \left[ 0.94 \left( \eta U_0 \right)^{2/3} \right] \left[ \gamma_L^{1/6} (\rho g)^{1/2} \right] \]

\( (5.4) \)
where \( \eta \), \( U_0 \), \( \gamma_{LV} \), \( \rho \) and \( g \) are respectively the viscosity of the sol, substrate speed, sol-vapor surface tension, density of the sol and acceleration due to gravity.

### 5.2.2.2. Spin coating

Spin coating process is a more dynamic process than dip coating and is divided into four stages: deposition, spin-up, spin-off and evaporation as shown in figure 5.2. Deposition is the direct addition of the sol to the substrate surface, usually in excess of the actual coating amount. In the next stage, spin-up causes the excess liquid to flow radially outward, driven by centrifugal force. During spin-off stage, liquid flows to the perimeter of the substrate, eventually leaning as droplets. The uniform thin film thickness \( h \) is given by the formula [52]

\[
h = h_0 \sqrt{1 + 4 \rho \omega^2 h^2 t / 3 \eta}
\]

where \( h_0 \) is the initial thickness, \( t \) is the time, and \( \omega \) is the angular velocity. The main advantage of spin coating is the film uniformity due to balancing the induced centrifugal force (pushing outward) with the resistive viscosity force (pushing inward).

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Figure: 5.2: Stages of spin coating process
5.2.3. Dye encapsulation in sol-gel matrix

As mentioned earlier, sol-gel process is a method that is used for the room temperature production of ceramics especially glass. This type of glass, viz. sol-gel glass can be porous, where the porosity and hence the refractive index can be controlled over a wide range by adjusting the fabrication conditions such as temperature or pressure. The sol-gel method is a convenient way to synthesise a host matrix for organic and organometallic dopants [53]. The organic dye to be encapsulated is added to the sol after partial hydrolysis of the precursor. As the degree of poly condensation increases, the sol becomes viscous and solidifies. The process continuous during aging and a porous matrix is formed around the dye molecule, trapping it inside. The large surface area and ultrafine pores of the gel make the dye accessible to small diffusing analyte species (ammonia in the present case), which react with the dye and change its optical properties. The rigid cage structure of the xerogel restricts translational motion of the dye molecules and in addition, dye aggregation is prevented as the individual dye molecules exist in separate cages [54].
as shown in figure 5.3. Entrapment of sol-gel matrices is independent of the functionalities of the dye. Moreover, physical entrapment is functionally non-invasive and preserves the integrity and directional homogeneity of the dye surface microstructure. Another notable property of these hybrid materials is its refractive index, which is specifically important in the development of optical waveguides. Generally, the refractive index of these composites is low because of the low density of the sol-gel material. These features of the organically modified sol-gel matrix enable this technology to be utilized for various fiber optic chemical sensing applications.

5.3. Unclad EWFS for Ammonia gas detection

5.3.1. Introduction

The advantages of sol-gel derived thin films may be combined with those of optical fibers or waveguide to produce intrinsic evanescent wave sensors. As explained in chapter 2, when light is guided through an optical fiber, the evanescent field, which extends to the surrounding region decays exponentially with distance from the core-cladding interface. If the cladding of a certain region of the fiber is removed and that region is coated with an organic dye entrapped sol-gel thin film, the degree of the evanescent wave interaction is dependant on the refractive index of the coating material. The evanescent wave – sol-gel approach provides a very attractive route to chemical sensors, demanding only a simple dip coating of the required waveguide substrate. Because the interrogating light remains guided, no focusing or collection optics is required in the sensing region and considerable miniaturization is feasible. Furthermore, the versatility of the sol-gel process enables the optimization of the sensor parameters viz. sensitivity, response time, signal to noise ratio etc. by the control of sol-gel film properties such as coating length, thickness and porosity.
5.3.2. Experimental

5.3.2.1. Preparation of the sensing Element

A 35cm length of plastic clad silica fiber of 200µm core diameter and 0.22 numerical aperture is used for making the sensor element. The jacket and cladding of the fiber are removed from a length 8cm of the middle portion of the fiber. Then, the uncladded region is coated with porous SiO$_2$ matrix in which an ammonia sensitive dye is embedded by using sol gel technology.

![Diagram of the sol-gel technique](image)

**Figure 5.4. Equilibrium of two protonated forms of BCP**

TEOS is used as the precursor for the sol preparation since the refractive index of the porous silica film produced is less than that of the fiber core. The ammonia sensitive dye used in the present case is bromocresol purple (BCP), which is chemically more stable and is more resistant to oxidation than other indicators. BCP exists in three different forms out of which two are important and are shown in figure 5.4. The phenolic form predominates in basic conditions, whereas hydroquinonic form is dominant in low acid concentrations. A schematic diagram of the sol-gel technique for the fabrication of the sensitive layers on the middle unclad portion of the fiber is shown in the figure 5.5.
Figure 5.5: Schematic diagram of the sol gel technique for the deposition of sensitive layer.

a: stirred for 5 minutes; b: stirred for 10 minutes; c: stirred for 15 minutes:

TEOS, anhydrous ethanol, water and the indicator dye are mixed in the molar ratio 1:4:1:10^-4 at room temperature with the help of a magnetic stirrer. Ethanol acts as a common solvent for TEOS and water. The porous silica is coated on the unclad portion of the fiber using the dip coating technique with the aid of a microprocessor controlled stepper motor. Since the drawing speed of the fiber from the sol is directly proportional to the thin film thickness, we use an optimum speed of 100mm/minute.
and a thin film thickness of approximately 200nm for a single layer is obtained. Multilayer sol gel coating is used in the present investigation because multiple sol gel coating enhances the sensitivity of the sensor [34]. The second layer is coated over the first one only after the complete curing of the first one and the third layer is coated in the same fashion. A schematic representation of a two layer sol-gel coating on a multimode fiber is shown in figure 5.6. The coated fiber is then kept for two weeks so that the dye gets stabilized in the gel matrix. It is then washed in water to remove the excess and unbound dye. The fabricated sensitive layers proved to be resistant against dilute acids, alkaline solutions and organic solvents such as acetone or alcohol.

![Figure 5.6. Two layer sol gel coatings on a multimode fiber](image)

\[5.3.2.2. \text{Optical arrangement for sensor characterization}\]

A schematic diagram of the experimental set up used to characterize the ammonia gas sensor is shown in figure 5.7. The laser emission at 600nm from a diode laser is coupled to the optical fiber using a microscope objective having almost the same numerical aperture as that of the fiber. The light intensity at the output of the fiber is detected using an optical power meter (Metrologic 45-545), which in turn is interfaced to a computer. All the measurements are carried out using a Lab-VIEW set-up.
Figure 5.7: Schematic diagram of the experimental setup

5.3.3. Results and discussions

Figure 5.8 displays the absorption spectra of BCP dye doped in multi layer sol-gel thin film coated over a glass substrate under two different environments; before and just after ammonia gas exposure. During the exposure of ammonia gas, depending on the concentration of ammonia, the ammonia sensitive dye changes its colour from yellow to blue. The change in colour leads to an attenuation of the guided light at this wavelength or near to this wavelength. The maximum absorption peak is at 596nm and hence a diode laser emitting near this wavelength is used to power the present sensor.

Here also, the fundamental equation that deals with evanescent wave sensing by conventional unclad fiber is applicable. That is,
where $P_{\text{out}}$ is the output power, $P_{\text{in}}$ is the input power of the fiber, $N$ is the total number of modal groups where each value of $N$ represents a group of modes having the same penetration depth, $\alpha$ is the molar absorption coefficient, $\eta_v$ is the modal fractional power in the cladding for $v^{th}$ core mode and $l$ is the interaction length of the evanescent field with the absorbing species of concentration $C$.

![Absorption Spectra](image)

**Figure 5.8: Absorption spectra of Bromocresol Purple entrapped in porous SiO$_2$ matrix**

When light from red diode laser is launched into the fiber placed in the sensor cell, the evanescent wave penetrates into the surrounding medium (ammonia gas). Depending on the concentration of ammonia, the ammonia sensitive dye, BCP, entrapped in the multi layer sol-gel thin film on the fiber changes its color from yellow to blue and hence evanescent wave absorption increases at the operating...
wavelength. The attenuation of the guided light due to the absorption of its evanescent part in the sensitive layers is pictorially illustrated in figure 5.9.

![Diagram of light propagation through sol gel coated fiber](image)

**Figure 5.9: Light propagation through sol gel coated fiber**

![Graph showing variation of ammonia sensor output with various concentrations of ammonia gas](image)

**Figure 5.10. Variation of the ammonia sensor output with various concentrations of ammonia gas.**

The variation of the sensor output with various concentrations of ammonia gas is shown in Figure 5.10. The curve clearly shows that the present instrument can
measure the ammonia concentration even from 0.027 to 2.04 mM/Ltr. The suggested reaction sequence of ammonia with the indicator dye is a reversible deprotonization of the dye [33]. The reaction can be divided into three steps. The first step is the reaction of gaseous ammonia with water to ammonia hydroxide

\[ NH_3(g) + H_2O \rightleftharpoons NH_4^+OH^- \]  

(5.7)

The second step is the deprotonization of the dye by ammonium hydroxide to a modified form of the indicator dye and water

\[ NH_4^+OH^- + H^+ \text{Dye}^- \rightleftharpoons NH_4^+ \text{Dye}^- + H_2O \]  

(5.8)

The last step is the back reaction to the primary dye and ammonia

\[ NH_4^+ \text{Dye}^- \rightleftharpoons H^+ \text{Dye}^- + NH_3(g) \]  

(5.9)

Figure 5.11 shows the response of the sensor element to different concentrations of ammonia gas recorded using Lab-VIEW. It is observed that during the ammonia flow
the sensor output decreases and after some time (approximately 3 minutes) it reaches a steady state value depending on the concentration of the ammonia gas. The reversible nature of the sensing element is also studied and is shown in figure 5.12. In this figure, the graph corresponding to each concentration of ammonia gas has three regions; A, B and C. A and C regions correspond to the sensor output before and after ammonia gas exposure whereas region B represents the sensor output during ammonia gas exposure. From the reversible response curve of the ammonia sensor it is seen that for each concentration of ammonia gas, the sensor output decreases from region A during ammonia gas exposure and reaches a steady state region B after a few minutes (approximately 8 minutes) [55]. Then, if we stop the ammonia flow the sensor output increases and reaches almost the starting region A, which is due to the reverse reaction of the indicator dye. This reversible nature of the sensing element eliminates the difficulty of replacing the sensing fiber after each measurement.

Figure 5.12. Reversible response of the ammonia sensor
5.4. LPG in multimode fiber for Ammonia gas detection

Long period gratings (LPGs) are a relatively new class of fiber optic devices that act to couple light from the propagating fiber mode to cladding modes, producing a series of attenuation bands in the fiber transmission spectrum. The resonance wavelengths of the attenuation are sensitive to local environment experienced by the fiber. Hence, in this section, the studies on the evanescent wave absorption on long period grating (LPG) in multimode optical fibers to detect ammonia gas is discussed. The theory, principle and fabrication of evanescent wave LPG sensors are explained in detail in chapter 4 and hence are not included here.

Long periodic gratings are written in an unjacketed multimode, PCS fiber (200/380μm) by point-by-point method with UV irradiation (single shot 355nm) from a pulsed Nd – YAG laser (Spectra Physics GCR-170) operated in the Q-switched mode. This LPG region, which has a length of 10mm and periodicity of 100μm, acts as the sensing region. This area is coated with layers of porous SiO₂ matrix in which an ammonia sensitive dye BCP is embedded by using sol-gel.

Figure 5.13: Schematic diagram of the experimental setup
technology as discussed in section 5.3.2.1. of this chapter. A schematic diagram of the experimental set up that is used to characterize the ammonia gas sensor is shown in figure 5.13, which is the same as Figure 5.7 except for the sensing fiber. The sensing element is introduced into the glass tube through the holes provided at the sides so that grating region of the fiber is within the glass tube and remains straight.

Just as in the case of unclad evanescent wave fiber optic ammonia gas sensor, light from a red diode laser is launched into the fiber placed in the sensor cell. The evanescent wave in the LPG region, penetrate the cladding and escapes into the surrounding medium (ammonia gas). The ammonia sensitive dye, BCP, entrapped in the multi-layer sol-gel thin film on the fiber reversibly changes its color from yellow to blue and hence evanescent wave absorption takes place which increases with increase in concentration of ammonia. Figure 5.14 shows the variation of the sensor output with various concentrations of ammonia gas. It is seen that the dynamic range

![Figure 5.14. Response of the LPG ammonia sensor with different concentrations of ammonia gas](image-url)
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of the sensor is from 0.027 to 2.04 mM/Ltr, which is the same as that of unclad EWFS [56]. It is also observed that during the ammonia flow the sensor output decreases and after some time reaches a steady state value depending on the concentration of the ammonia gas. At this stage if the ammonia flow is stopped, the sensor output increases and reaches almost to the original value recorded before ammonia gas exposure. This reveals the reversibility of the sensor. The response time and the recovery time of this sensor are approximately 3 and 8 minutes respectively, which are same as that in the case of the unclad EWFS discussed in the previous section. However, the main attraction of the present sensor is that the sensing length is only 1 cm, which is very small compared with that of the conventional evanescent wave approach.
Design and fabrication of fiber optic sensors

References