Semicontacting polymer thin film sensors for detection of toxic gases

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The development of efficient devices for detection of toxic gases in the environment is an important challenge in the area of sensor development. The selection of proper material to act as a selective interface to mediate between the outside environment and the sensor transducer is very crucial. The recent development of semiconducting polymer materials, with every imaginable combination of physical and chemical characteristics for fabrication of sensors has led to the fabrication of efficient gas sensors. The diversity of properties of these polymers enables them to provide a wide range of applications in sensor technology. These polymers do not suffer from the drawbacks of preparation complications and synthesis complexities and have a long shelf-life and efficiency. A method of large-scale production of a new class of sensing polymers, the semiconducting polymers is described in this paper. The sensors show excellent sensitivity in the thin film form. The thin films are prepared by vacuum deposition method, hence a reliance on a dry technology. These sensors find applications in industrial, technological, medical, civilian and strategic sector. This has led to the development of low cost, efficient and simple to operate sensor devices that can be positioned remotely and can be used for on-line monitoring. Semiconducting polymeric thin film sensors are the latest devices to be used for the above mentioned applications and have been tested for their efficiency, reliability, cost effectiveness and performance.

The most important advantage of these polymeric sensors is their room temperature operation and high sensitivity.

1 Introduction

Life and environment are interdependent. The plant and animal life is affected by various environment factors, in turn these lives modify their environment in many ways. Man himself is no exception to it and is involved in a tremendous struggle against the pollution of the environment. The pollution has become a major threat to our existence especially to the industrialized or developing countries. The pollution from various sources has gone to such an extent that the human beings are unable to breathe fresh air. The environmental pollution is an unfavourable alteration of our surroundings, wholly or largely as a byproduct of our actions through direct or indirect effects of changes in air quality around us. The earth is surrounded by air cover up to a height of 1.5 km from the surface of the earth, a reservoir containing $5 \times 10^{19}$ km³ of air. The air contains gases like oxygen 21 %, nitrogen 78 %, carbon-dioxide 0.3%, hydrogen, etc. in a fixed ratio. Whenever due to certain reasons the concentration of gases other than oxygen reaches a value more than specified above, it becomes life threatening and this phenomenon is called pollution. This may happen due to various reasons, for example smoke and grit, exhaust gases, ionizing radiation, radioactive elements, biocides and pesticides and photo-chemical smog, etc. This problem becomes more grave in modern cities and industrial environment, where there is limited space for the person to work around. Hence a constant vigil on the air quality is essential. Therefore monitoring and management of air quality is of direct concern to everyone living in the industrialized nations of the world\(^{10}\). The economic and social activities of a modern society lead to emissions from a multitude of sources that effect air quality. These emissions take the form of toxic gases and microbiological activity, both of which have well documented effects on human, animal and plant health when their levels are too high. Air quality is of distributed problem. Point measurements of emissions at the source are very much essential to ascertain the air quality. This is required for monitoring the environment in the cities, where vehicular pollution is the major source of concern, producing carbon monoxide beyond health hazard thresholds and in the mines as well, where a continuous monitoring of carbon monoxide level is essential. The same is valid for HCN level in industry, where this problem is frequently encountered. The detection of hazardous microbiological species and bacteria called pathogens present in the air and in the workspace that could cause disease is equally important. There are several techniques available for sensing the air quality. The presently available techniques like passive spectrophotometric techniques are
used for wide area mapping of the atmosphere. These techniques provide very wide, even global, coverage but rather limited special resolution and have limited use in addressing air quality issues. The sensing ability to map the atmosphere in the working space and time allows us to include the effects of transport and thereby to strike a better balance between cost and benefit, as we make an important decision about the management of air quality and toxicity including presence of microorganisms in atmosphere and environment, particularly in semiconductor industry, coal mines, food processing and places concerning health conditions like those in hospitals. This capability is exemplified by physical sensing and measurement systems, i.e. systems able to detect and measure parameters related to monitoring of environment. Smart sensors are incorporated extensively into measuring and control systems. It has become apparent that more sophisticated measurement devices are necessary to collect the information, which can be processed in new management system. As the possibilities of such systems increases, the role of sensors, acting as primary units in information perception, rises considerably and demand for them automation and robot technology, and gain an increasingly greater significance as structural elements of systems. This new generation of sensors will become an integral part of collection and control systems in nearly every industry and market place. Most generally speaking, sensors are devices, which convert physical or chemical quantities into electrical signal, which are convenient to use. The sensor carries out a quantitative conversion of a certain property of the substance or the process. The property which is registered quantitatively may be detected in a number of ways and it may have a physical (e.g. mechanical, thermal, electromagnetic etc.) or a chemical nature. In accordance with its principle of operation, the sensor converts the property into an electrically assessable value, which can be transmitted further in the sensor system for assessment or indication.

A sensor should possess the following characteristics:

1. **Specificity for the target species** — This means that fluctuations in the signal obtained can be unambiguously assigned to the target species. A large amount of sensor research has been directed towards developing selective sensors and to devise efficient methods for quantifying selectivity, so that the limitations of applicability of a particular device can be clearly identified.

2. **Sensitivity to charges in target species and concentration** — The response slope of the sensor should be as larger as possible to enable very small changes in the target species concentration to be detected. The sensor should be very specific and selective for responding to the particular species for which it has been designed, in presence of many interfering species present around.

3. **An extremely fast (instantaneous) response time** — These enable high-speed fluctuations in concentration to be monitored. For many applications, time constant may be of the order of a few seconds.

4. **Sensor operating temperature** — The most important is the sensor operating temperature. Most of the sensors available commercially operate at elevated temperatures up to 300 °C. This puts a limitation on their operation and positioning at remote places. This also includes another step in the fabrication of the sensor for providing a healthy facility along with the sensing element. This in turn makes provision for extra electronic circuitry to be provided with sensor microprocessor. The heating of the sensing element also puts a limitation on the life of the sensing material and hence its lifetime.

5. **Lifetime and shelf life** — This is an important characteristic of the sensors, particularly for those meant for detection of toxic gases. The gradual reactions between the sensor material and the toxic gases cause their deterioration. However, devices such as polymer based sensors can have lifetimes extending into years, owing to the reversibility and physical adsorption of the effluent on the sensor.

6. **Small size and high precision** — The tendency to integrate semiconductor manufacturing technologies with sensor fabrication is an important aspect. The sensing devices should be small, solid state, well characterized and identical in performance. They should also be able to function as sensor arrays as well as single devices. Advancement in the areas of electronics and computing have enabled powerful signal processing facilities to be made available in small palm top instruments linked to sensor arrays.

7. **Cost effectiveness** — The economy of the process and abundance and easy availability of the raw material used for fabrication of sensor is an important aspect of the sensor technology.

8. **Possibility of remote positioning** — It should be possible for the sensor to be positioned at remote places like mines, semiconductor processing line, food processing chain, etc. have an on-line monitoring of the site.
This can be achieved by miniaturizing the sensor device and using advanced electronic circuitry for communication with the monitor module.

There had been a tremendous amount of research in last 15 years, in the area of development of various types of sensors, recently termed as smart materials and smart sensors. However the currently available sensors that have come out because of the above mentioned efforts are the inorganic materials based sensors. There have been efforts to incorporate new materials for chemical process applications, like detection of quality of fresh tomatoes from irradiated tomatoes, for detection of coffee odour. A multi-sensor system based on tin oxide has been prepared for detection of alcohol and for monitoring the quality of fish and cod fillets, for a large variety of spirits, enzymes and microbial sensors comprising of immobilized microorganisms and electrochemical devices for detection of organic compounds produced in fermentation. Most of these sensors operate at temperatures in the range of 250-300 °C. This eventually puts a limitation to their extensive and actual use for at the site monitoring. Owing to this reason, there has been an intensive effort to look for advanced materials, which can be used for preparation of fast response, room temperature operating sensors having high selectivity and sensitivity. The most commonly reported organic material is pthalocyanine. However, this type of sensors too operate at 150 °C.

2 Fabrication of Polymeric Thin Film Sensors

The polymeric thin film sensors were prepared in a batch production process. First, a co-polymer of aniline and formaldehyde was prepared by adding aniline monomer in dilute hydrochloric acid. To this solution, a formaldehyde solution was added with constant stirring. The resultant solution was allowed to stand for a specific time and then the particular dopant was added. The resultant solution was stirred for 30 min and then poured into 15-20% NaOH solution. The precipitate obtained was filtered, washed with distilled water until the filtrate is free from alkali and dried in oven. The powder so obtained was used for fabrication of pellets and for preparation of polymeric films by vacuum evaporation on glass substrate. Sensors based on undoped and doped polymeric pellets were prepared. The vacuum deposited gold contacts were provided to these thin films. The I-V characteristics of these samples and upon exposure to toxic gases and microorganisms were measured in metal/polymer/metal sandwich and lateral structural configuration. The specific change in current-voltage characteristics is utilized for the identification of type of gases and microorganisms and their concentration. Polymeric thin film sensors prepared by doping Cu and Al were found sensitive to HCN. Polymeric thin film sensors having Fe and Al as dopants were found sensitive to carbon monoxide. For detection of microorganisms the dopants were varied and various concentrations of Fe, Al, and Cu were utilized for obtaining the specificity and selectivity. Fig. 1 shows the process flow chart for large-scale production of polyaniline thin film sensors.

3 Results and Discussion

The current-voltage characteristics of the polymeric thin film doped with particular dopants were obtained without and with exposure to various gases and microorganisms. The operating voltage for sensor was 1.54 V. The particular doping combination in the polymer makes the sensor specific for a particular species. A sensor responding maximum to a particular gas/microorganism does not respond to other species. The sensitivity is described as the ratio of the magnitude of current increase upon exposure to the toxic gas/microorganism (I_e) to that of without exposure to the microorganism (I_a).

\[ S = \left( \frac{I_e}{I_a} \right) \]

Fig. 1 — The process flow chart for large-scale production of polyaniline thin film sensors.
Table 1 shows the performance specifications of the polyaniline thin film sensors for detection of HCN and carbon monoxide.

4 Theory Of Semiconducting Polyamine Thin Film Sensors

It has been observed that the polyaniline thin films have higher sensitivity than the polyaniline bulk pellets, due to the large surface-to-volume ratio in thin films. The response of the sensor increases with the concentration of the CO gas (Fig. 2).

While upon exposure to HCN the sensor response decreases (Fig. 3), the slope of the variation is the opposite in the two cases. The slope of the variation is measured and utilized for quantification of the concentration after optimization of sensor parameters. The sensor operation is reversible. There is a rise in output current from the sensor as it is exposed to the gas/microorganisms. The sensors return to its original state as soon as the toxic gas/microorganism is removed. When the sensor is removed from the gas/microbiological environment, the output decreases to a minimum value and the sensor recovers to the original state in 8-10 s.

The results can be explained on the basis of change in the concentration of charge carriers around the polymeric thin films, upon exposure to toxic gases, which in turn affect the I-V characteristics. As the sensor is reusable, it can be assumed that there is no chemical reaction between the polymer and the toxic gases. The interaction between the polyaniline thin films and the toxic gases can be explained by taking into account the interaction between the ions and molecules of the toxic gas with the polyaniline thin films. From the scanning electron micrograph of the polyaniline thin film, it has been observed that polyaniline thin films prepared by vacuum evaporation techniques and compensated by dopants have a strong degree of crystallinity (Fig. 4). The undoped polyaniline and their thin films are electrically non-conducting. The vacuum deposited polyaniline thin films are semiconducting and the corresponding energy band diagram is shown in Fig. 5.
It is known that polyaniline is a $p$-type semiconductor and the conduction in polyaniline thin films is due to the hopping transport of polarons and bipolarons, which are delocalized over a few molecular units. The polarons and bipolarons become mobilized under the action of electric field in a sensor configuration. These charge carriers move intra-chain, inter-chain and through inter-crystallites. The conduction in polyaniline thin film occurs by crossing over of the charge carriers through the inter-crystallite boundaries, which offer a charge barrier. This makes the polyaniline vacuum deposited film to become semi-conducting. When the thin films are exposed to gases like carbon monoxide, they result in a reduction of the barrier height at the inter-crystallite grain boundary, thus lowering the inter-crystallite barrier (Fig. 6). This increases the current flow through the sensor. Hence, there is an increase in the current output from the sensor. The lowering of the barrier height is directly proportional to the amount of the gas absorbed by the thin film and hence the increase in the sensor output. This is evident from Fig. 2. When the sensor is exposed to gases like HCN, the effect of the absorption of the HCN is to increase the barrier height of the inter-crystallite barrier, thereby reducing the current.

![Energy band diagram of polyaniline thin films upon exposure to CO](image)

![Energy band diagram of vacuum deposited semiconducting polyaniline thin films](image)

![Energy band diagram of polyaniline thin films upon exposure to HCN](image)
(Fig. 7). The slope thus becomes negative (Fig. 3). This makes the sensor response and activity very selective and specific. A similar process occurs during the interaction of microorganisms with the polyaniline thin films. The response from the sensors and the slope is a measure of the type and concentration of the microorganism.

These sensors have been tested for E. Coli, a bacteria causing diarrhoea and gastroenteritis and for Geotrichum Candidum, a bacteria, causing butter spoilage and food poisoning. The above proposed model taking into account the reaction at the gas/microorganism-polymer film interface has further been supported by capacitance measurements of the interface with and without presence of the interacting species. The dielectric capacitance and dielectric losses at the interface have been observed to be strongly affected by the exposure to gas/microorganisms.

5 Conclusion

Vacuum deposited polyaniline thin film sensors have been prepared for detection of toxic gases and a biological species in environment, coal mines, semiconductor industry and medical applications and food processing industry. The behavioural acceptance tests have shown that the sensors are highly specific, selective and cost effective. The sensitivity of the sensors is high and detection limit is low. The stability, reproducibility and shelf life are excellent. A model has been proposed for the sensing mechanism in polyaniline thin films.

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