Development of CSA doped PANi-Ta_2O_5 based Chemiresistors and OFETs for NO_2 gas detection at room temperature

Chapter 1

Introduction

Because of the fast industrialization, spikes in population growth, unprecedented rise in vehicles, emission of harmful gases every day, today we see a grim world scenario with deteriorating ecology, and imperiled human lives. The incessant exudation of dangerous industrial outflow has posed a serious threat to the very existence of all life forms. Keeping this in view, there is indeed an urgent need to detect and monitor the levels of the disastrous effluents as an immediate security measure to the environment and the living beings.

1.1Nitrogen dioxide (NO_2) as a threat to human lives and environment

Nitrogen oxides represent the group of seven gases and compounds consisted of nitrogen and oxygen, and are collectively known as NO_x gases. The two most common hazardous forms are nitric oxide and nitrogen dioxide. Nitrous oxide, commonly known as laughing gas, is a greenhouse gas that plays an alarming role in global warming. Nitrogen dioxide is used as the most weighted indicator of the NO_x family and is considered as the most threatening one to human lives and the environment.

Nitrogen dioxide (NO_2) is a reddish-brown toxic gas with a characteristic pungent, choking odour and is a prominent air pollutant, and a hazardous gas to human health. NO_2 is an intermediate product in the industrial synthesis of nitric acid, millions of tons of which are produced every year. The most important source of NO_2 is the operation of motor vehicles, internal combustion engines and thermal power stations. Fuel-burning appliances, like home heaters and gas stoves, produce large amounts of NO_2 in indoor set-ups. NO_2 also reacts with volatile organic compounds in the presence of sunlight to form ozone, which is harmful to human health and ecology of the surrounding.

The American and European countries are among the largest producers of NO_2 with massive numbers of industries. But according to reports produced by NASA (National Aeronautics and Space Administration), these regions have been succeeded in dramatic reduction of the production of this toxic gas between the years of 2005 to 2014.

The other part of the story is dismal. NASA said South Asian developing countries like India are contributing largely to the increasing production of NO_2 everyday with high rise economy, industries like petrochemical complexes, refineries, factories and infrastructure development.

Effect of human health to prolonged exposure to NO_2 is highly aggravated. Breathing in air with high concentration of NO_2 can damage human respiratory system. Respiratory diseases like asthma can further deteriorate under the influence of NO_2. People with asthma complaints, children and elderly are quite susceptible to the dangerous effects of NO_2 exposure.

The environment also has faced numerous adverse effects due to the presence of NO_2. NO_2 and other forms of NOx react with water, oxygen and other chemicals present in the environment to produce acid rain. Acid rain is harmful to the sensitive ecosystem such as the water bodies and forests. NO_2 and other NO_x compounds present in the atmosphere also can cause nutrient pollution in coastal water as cited in an article published by *united states environmental protection agency*.

The nitrate particles emanated from NO_2 make the air foggy. Even in bright sunny days, many industrially busy cities wear a rather dusky look and it becomes difficult to look through (Fig.1.1). Even the national parks we visit witness similar situation.

According to a report published by *Greenpeace Southeast Asia* and *Daily News and Analysis* report, it is stated that air pollution in Delhi, India’s national capital caused a toll of around 24000 lives and 5.8% GDP fall in the first half of of 2020. This picture has emerged even after the citizens kept mostly indoors due to COVID-19 lockdown since March, 2020.

Fig. 1.1. A morning time with smoky haze spreading over parts of New Delhi, India [*photo courtesy: daily news and analysis*].

This situation is undoubtedly detrimental to the very existence of living beings and to the sustenance of ecological balance. Keeping in view of all these factors, it is important to have precise and adequate information about the level of the poisonous gas in the surrounding atmosphere and thereby, devise appropriate measures to improve the scenario.

1.2 Gas sensors

Gas sensors belong to a broader category of chemical sensors. The chemical sensor is a device that responds to a particular target in a selective and reversible way, and transforms the input chemical quantity such as the concentration of the sample or a total composition analysis, into quantitative unit of electrical signal as illustrated in Fig. 1.2. The chemical information may evolve from a chemical reaction by a chemical compound or a biomaterial attached onto the transducer's surface towards an analyte [1].

The gas sensors have been considered as an effective sensor technology in the detection of various environmentally toxic gases present at a low concentration level. A gas sensor is a sensing device that can measure the presence and/or concentration of an analyte gas in a given environment. The gas sensors work on the principle that when the sensing receptor comes in contact with the target gas molecule, a potential difference or change in current takes place. This gives a measure of the presence of the target gas.

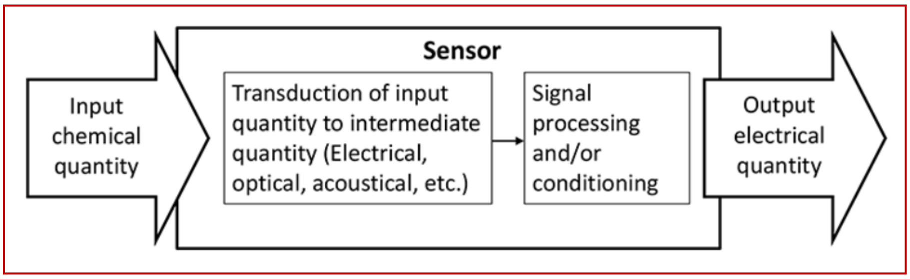

Fig.1.2. Sensor's working principle- schematic diagram of a sensor that produces an electrical output in response to the presence of an input quantity [1].

Gas sensors have become very demanding and promising means to detect the presence of poisonous gases owing to their host of advantages such as satisfactory sensor response, low cost, small size, portability, ease of large-scale production and environment-friendly nature.

Gas sensors or chemical sensors play a pivotal role in monitoring environmentally pollutant gases in air, water and soil. Environmental contaminants like organic dyes, bacteria or fungi present in food, textile and leather industries need also to be monitored.

Modern gas sensors also occupy an important place in our daily lives. It can be found at our homes to monitor the level of carbon monoxide (CO) produced by common home appliances such as gas or oil furnaces, gas water heaters, fireplaces, charcoal grills etc. They are used at our work place to check the levels of toxic gases and odors and in health units to monitor the anaesthetic and respiratory gases. In industries, gas sensors are employed to monitor the leakage of toxic and explosive gases. There has been increasing demand of gas sensors, particularly in the work places which require safe working environment with tough government safety norms being imposed.

Keeping in pace with demand, developing countries like India can see several niche markets emerging for the mass manufacture of low-cost (<=INR 500 per unit), low-power (mW or less) gas sensors to be employed in notebooks, tablets, mobile phones and other portable on-chip devices. However, the average cost of a gas sensor available today in an Indian market is around INR 1500. The increase in cost is due to the additional cost involved in the discrete components and the interface circuitry used to monitor sensor outputs and heating temperature. They are manufactured in small volumes which add the extra cost. The recent market has seen improved growth with reduced unit cost of the sensors through the development of small-sized devices. The semiconductor based gas sensors as opposed to electrochemical gas sensors are manufactured based on complementary metal oxide semiconductor (CMOS) chip combined with associated microelectromechanical systems (MEMS) based circuitry. This has made the process viable for low cost and high-volume manufacturing [2].

At present, important application areas of gas sensors are industrial and automotive sectors to detect NOx, NH_3, CO_2, SO_2, O_2, O_3, hydrocarbons etc., the food industries to control the fermentation process, domestic sectors to detect CO, humidity and other combustible gases, in medical sectors for patient monitoring and diagnostics, and in security fields to detect the presence of explosives [3].

Monitoring and recording the changes in the surrounding atmosphere triggered by the presence of dangerous chemical stimuli have become an urgent need for the safety of human lives and future production. This goal can be achieved with the development of high-performance sensors which are capable of detecting the environmentally harmful gases, both volatile and non-volatile types, at a lower concentration level, with closed-loop controlling in diverse fields including production units, food industry, health, public security, environmental monitoring and agriculture.

1.2.1 Types of gas sensors

Gas sensors can be classified on the basis of their working principle such as conductivity gas sensors, piezoelectric gas sensors, electrochemical gas sensors, metal-oxide-semiconductor field effect transistors (MOSFET) and optical gas sensors.

a) Conductivity gas sensors

The conductivity gas sensors are the most commonly used sensors because of their relatively simple interface circuits. They are low-cost devices and are capable of providing high sensitivity and selectivity.

These sensors use the principle which involves a change in some property of the sensing material caused by the exposure to a gas or odour which subsequently results in a change in resistance in the device. The mechanism which results in the change in resistance differs for each material. The general schematic of a conductivity gas sensor is shown in Fig.1.3.

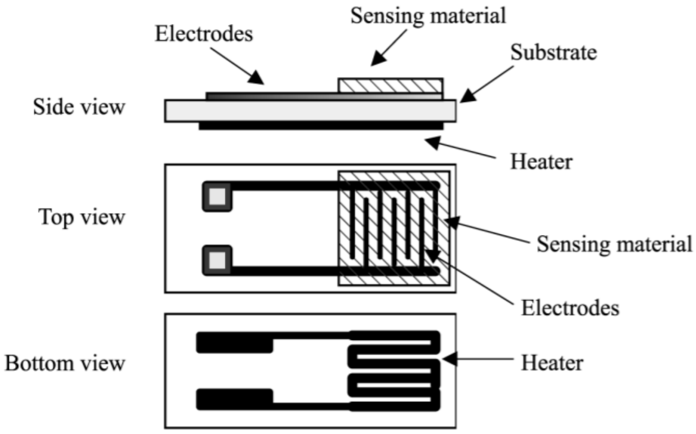

Fig. 1.3. General structure of a typical conductivity gas sensor [4].

Metal-oxide conductive sensors constitute a large category of commercially used sensors due to their high gas sensitivity. The gas sensing mechanism is based on the change in resistance of the oxide on interaction with the analyte gas and the change is normally proportional to the concentration of the gas. The n-type metal oxide sensors use zinc oxide, tin dioxide, iron (III) oxide or titanium dioxide and respond to reducing gases. The p-type sensors use nickel oxide, cobalt oxide and respond to oxidizing gases [4].

Metal-oxide sensors usually operate at a high temperature and require heating system to maintain the particular operating temperature. This leads to high power consumption and shorter life-time. Also, CMOS circuitry and the front-end MEMS unit used by the sensors involve complex fabrication technique [5].

Conducting polymer/conducting polymer (CP) composite based gas sensors constitute another promising class of conductivity type gas sensors with their room temperature operability and easy fabrication process. Here, the sensing material can be deposited between the two electrodes by simpler deposition techniques. The sensor device can be manufactured by employing standard photolithography techniques [5]. The research and development of CP based gas sensors have attained a pinnacle of success driven by easy but novel processing technology based on nanoscience and nanotechnology. This involves primarily bottom-to-top fabrication techniques resulting in overall low production cost. CP based nanostructures have emerged as the potential candidate of sensing material due to their tunable properties, compact size, high surface-to-volume ratio, plenty of available surface active sites, benefits of crystallnity aspects leading to high surface reactivity [3]. The CP based gas sensor is the subject of study of the current research work.

b) Piezoelectric gas sensors

Piezoelectric gas sensors include surface acoustic wave (SAW), quartz crystal microbalance (QCM) and bulk acoustic wave (BAW) sensors. Their working principle rests on the fact that a change in the mass of the piezoelectric layer due to the absorption of gas molecules causes a change in the resonant frequency on a vapour exposure. These sensors can show high selectivity and very fast response time, and are highly researched in the area of sensor array applications. However, they suffer from some disadvantages such as complexity involved in the fabrication process and the interface circuitry, difficulty in batch–to-batch reproducibility and replacement process of the damaged components [4]. The schematic of piezoelectric SAW based gas sensor is shown in Fig.1.4.

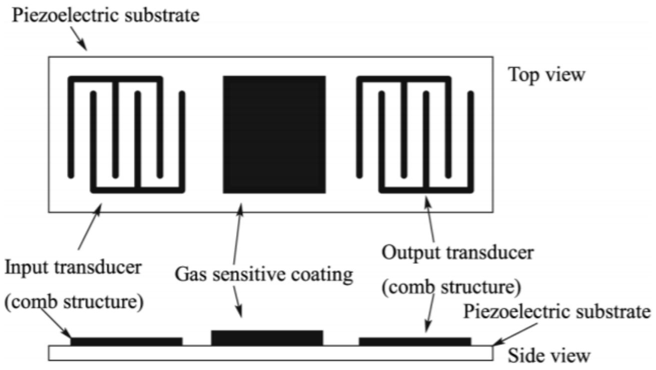

Fig.1.4 Schematic of a SAW sensor [4].

c) Electrochemical gas sensors

Another commonly implemented gas sensor category is the electrochemical sensors. The electrochemical cell used by these sensors is either amperometric or potentiometric type. The basic structure of two-electrode electrochemical sensor is the working electrode which acts as the sensing electrode, a counter electrode and an ion conductor (electrolyte) in between them [6]. The most commonly used electrolyte is a mineral acid, but many applications use organic type electrolytes also.

In both types of the above sensors, the analyte gas diffuses into the working electrode to reach the sensing area of the device through a porous membrane. The gas reacts by oxidation or reduction on the electrode, producing an electric current, which is measured as a signal by an external circuit. If oxidation takes place at the working electrode, reduction takes place at the counter electrode [7]. A simplified schematic of electrochemical sensor is presented in Fig.1.5.

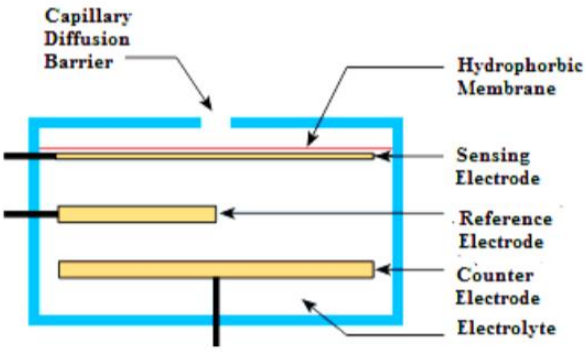

Fig. 1.5. Schematic of electrochemical sensor [8].

The electrochemical gas sensing works on gas oxidation and reducing mechanisms on the sensing surface with catalytic potential, which causes significant change in charge transfer. This change can be amplified and produced as a signal. The electrochemical sesnors are reliable, cost-effective, fast and small. Therefore, they are suitable for automotive sectors and residential areas for gas detection [7]. Important disadvantages of these sensors include cross sensitivity to interfering gases and limited life time. They cannot be used to detect the gases which are electrochemically active. They show extreme sensitivity to temperature fluctuations [9].

Although the electrochemical sensors come with low cost, it is not possible to integrate the sensor circuit and other components on the same chip. This is because they require quite a large amount of liquid electrolytes and non-CMOS catalytic materials such as silver or platinum electrodes [2].

d) MOSFET based gas sensors

MOSFET based gas sensors are mainly applied to detect the analyte gas through redox reactions between the gas and the metal oxide surface. This causes electronic variations of the oxide surface which is transduced into a change in electrical resistance. The resistance variation could be measured by finding the change in capacitance, work function, optical properties, mass or reaction energy [10]. The operation of MOSFET based gas sensors is discussed in chapter 4.

Although MOSFET based sensors represent a vast category of commercially used sensors due to their high gas sensitivity, low cost and simplicity [11], they usually operate at a high temperature which leads to short longevity. MOSFET based gas sensors usually operate at a temperature above 100^0C and are limited to a range of 175^0-200^0C due to the use of the silicon technology [12]. Their circuitry requires heating system to maintain the particular operating temperature.

e) Optical gas sensors

Optical gas sensors employ optical methods using spectroscopy techniques. These methods include non-absorption techniques such as Gas Chemiluminescence (CL) and absorption techniques such as Non-Dispersive Infrared (NDIR) [13]. The gas sensing principle of optical sensors and their schematics are shown in Fig.1.6.

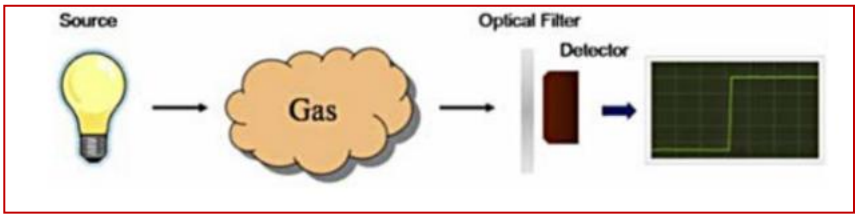

Fig. 1.6.a) Gas sensing principle of optical sensors [13].

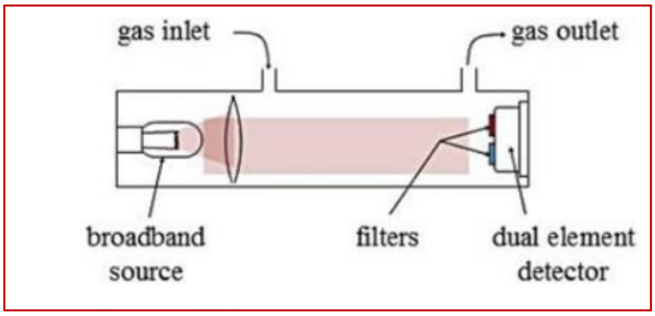

Fig. 1.6.b) Simplified schematic of a NDIR optical gas sensor [13].

Optical sensors are capable of rendering higher gas sensitivity, selectivity and longer life-time than those using non-optical methods.Their response time is faster which makes them suitable for on-line real time gas detection. However, their use in gas sensing has been restricted due to miniaturization and high cost [10].

1.2.2 NO_2 gas sensors

As discussed above, nitrogen dioxide (NO_2) is a prominent air pollutant contributing to the life-threatening effects in the environment. A major amount of the gas is produced and released each year from combustion and automotive emissions. Thus, the need for NO_2 gas sensors, preferably in cost-effective, light weight, efficient form has become inevitable. There is growing demand to install at the sites the sensors where the amount of NO_2 can escalate to a precarious level, particularly in industries, waste incinerators and vehicles.Typical applications where dangerous level of NO_2 needs immediate attention and can benefit from a NO_2 gas detector are combustion sources, power stations, pulp mills, butane stoves etc.

The inimical effects of NO_2 emission in environment and public health have opened up doors of extensive research and triggered immense technological progress in the field of NO_2 gas sensors. A wide variety of NO_2 gas sensors are commercially available today. They are metal-oxide based resistive, electrochemical and optical sensors [14], [15]. Optical sensors provide high sensitivity using unique optical portrayal of NO_2 molecules but they come with large size and high cost. Electrochemical sensors rely on electrochemical reduction between the catalysts and NO_2 molecules. They are cost-effective but have a shorter life span. Resistive sensors work on the principle of charge transfer between the metal-oxide layer and NO_2 molecules absorbed, with low selectivity and high operating temperature [16].

An ideal gas sensor is expected to possess high sensor response, good selectivity, fast response and recovery time, high stability and repeatability, room-temperature operability, easy fabrication and low cost for practical applications. To meet these parameters, different NO_2 gas sensors are being widely researched based on various transduction principles, e.g., solid-state electrochemical sensor, quartz-crystal microbalance (QCM), capacitive sensors, surface acoustic wave (SAW), chemi-resistors, field-effect transistors [17].

On the realm of fast developing sensor technologies, chemiresistive sensors and organic field-effect transistors (OFETs) have attracted enormous attention owing to their plentiful advantages such as easy synthesis and fabrication process, low cost and room temperature operability. These sensors evolved as very promising due to the use of organic semiconductors (OSCs) as the sensing material. The OSCs are based on conducting polymers (CPs) including conjugated polymers such as polyacetylene, polythiophene (PTh), polypyrrole (Ppy), polyaniline (PANi), poly(3,4-ethylenedioxythiophene (PEDOT) and small molecules such as pentacene, tertracene, rubrene. Most fascinating aspect of the CPs is that their molecular compostion can be fine tuned by blending them with various organic/inorganic counterparts to achieve the desired outcome.

1.3 Conducting Polymers (CPs)

Conducting polymers (CPs) were discovered in the year 1977 [18] and since then they were researched extensively in numerous fields of interest. In the year 2000, MacDiarmed, Heeger and Shirakawa jointly received Nobel Prize in chemistry for the discovery and development of CPs which had significant applications in the field of microelectronics. This had opened up an immense surge of research on CPs to exploit their enormous potential. The year 2000 was also the year of emergence and beginning of the era of nanoscience and nanotechnology. This triggered the dawn of CP nanomaterials and overpouring research to witness their several impressive novel properties.

CPs possess several notable advantages such as flexible electrical and electronic properties, easy synthesis process, non-corrosiveness, lighter weight and low cost [19]. These aspects have made them very suitable in diverse portfolio of applications such as microelectronics, opto-electronics, electro-chemical capacitors, actuators, gas sensing etc. Several past works established CPs to be a very effective material in the gas sensing field [20]. However, CPs have some inherent disadvantages like low solubility, relatively low conductivity, low thermal stability, inferior long-term stability. The low conductivity of the CPs has limited their use in the fields of transistors and memory devices [21]. However, conductivity of CPs can be improved to a great extent by means of doping or protonation. In the gas sensing area, pure CPs exhibit low sensor response, poor reproducibility, short life-span. Also, due to its highly inflexible backbone chain, most of the CPs are insoluble and infusible [22]. To mitigate many of these problems, CPs are often functionalised as hybrid material by incorporating inorganic metal/metal oxides into the polymer matrix to address the shortcomings [19].

Polyacetylene (PA) was the first CP discovered by the American scientists MacDiarmid and Heeger, and their Japanese colleague Shirakawa in 1977 as mentioned earlier. Although PA was found as highly conductive, it was pretty unstable and could easily degrade by oxidative reactions. This led PA unsuitable for use in electronic devices and batteries. Since then numerous other CPs similar to PA were extensively researched incorporating doping level ranging from insulators to metals. The chemical structures of various popularly implemented conducting polymers such as polyacetylene, polythiophene (PTh), polypyrrole (Ppy), polyaniline (PANi), poly(3,4- ethylenedioxythiophene (PEDOT) are shown in Fig. 1.7.

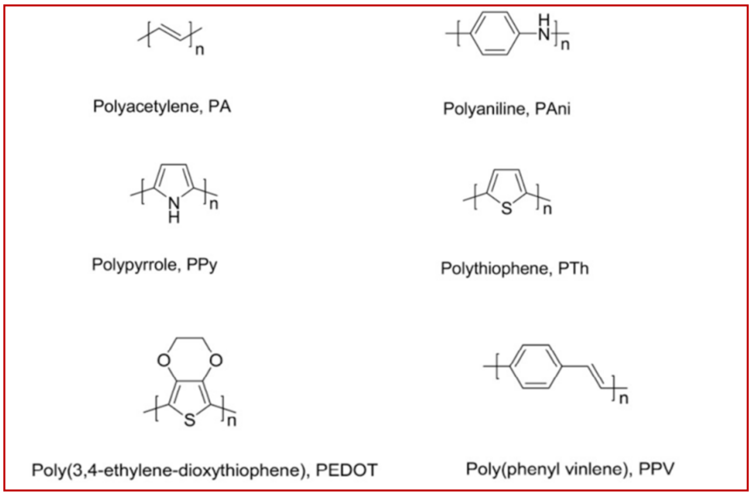

Fig.1.7. Chemical structure of some commonly used conducting polymers [20].

CPs are characterized by alternating single and double bonds along the polymer backbone (conjugation). Due to conjugation along the polymer chain, electrons are delocalized and wander about the whole system. These delocalized electrons act as the charge carriers to turn the polymers into conductive form and cause the formation of anions and cations. Under the influence of an external electrical field, the anions and cations hop from one site to another, increasing the conductivity. The process of doping allows the formation of conduction band in the polymer structure and causes the electrons to flow [23].The CPs demonstrate comparatively lower conductivity (less than 10^2 S/cm and 10^4 S/cm for polyacetylene) and hence are categorised as semiconductors (organic semiconductors) rather than metals [24].

Charge carriers must be added to the CPs due to their intrinsically low charge carrier densities. This is achieved by injection, photo carrier generation, or doping. The characteristic low mobility and disordered nature of the materials are issues for charge carrier transport through the material. Organic semiconductors like PANi can typically transport one type of charge carrier more easily. Most of the CPs behave as p-type materials and if ambipolar transport is observed, hole mobility is usually orders of magnitudes higher than electron mobility. This is attributed to traps exist in the material that hinder the electron transport [25].

CPs are doped using various methods to achieve improved conductivity. Dopants in the polymer involve redox reactions in which charges are transferred with subsequent formation of charge carriers. The dopant not only withdraws electrons from the CP but also adds electrons to the CP backbone. Due to doping, electrons are extracted from the highest occupied molecular orbital (HOMO) or the valence band (oxidation), or transferred to the lowest unoccupied molecular orbital (LUMO) or the conduction band (reduction). This oxidation and reduction processes create charge carriers in the form of polarons, bipolarons or solitons in the polymer which finally contributes to the conduction process [26].

1.4 CPs in gas sensing

Since their discovery, the unique properties of the CPs such as mechanical flexibility, low cost and light weight, and tailor-made molecular structure have swayed in a revolutionary wave in the field of gas sensing. The use of CPs as the sensing material to detect a host of environmentally toxic gases and volatile organic compounds (VOCs) at ambient conditions and at a very low concentration has been a breakthrough in the fields of environmental monitoring, health and industrial quality control.

Particular interest is focussed on utilizing nanostructured CPs in gas sensing sectors for their enhanced surface-to-volume ratio, and unique electrical and physical properties compared to their bulk counterpart. They can be easily functionalised with a large variety of functional groups to respond more effectively to the target gas even at a trace amount. On exposure to the target gas, their response mechanism undergoes chemical and mechanical interactions including oxidation/reduction and charge transfer. The doping and oxidation levels, elongation of conjugation length are the key factors which cause delocalization of the π-electrons. These intrinsic factors are crucial for designing high performance CP based gas sensors [27].

1.5 Use of Organic-inorganic hybrid nanocomposites in gas sensing

The class of nanocomposite based on CPs and inorganic materials is a fast growing area of research, particularly in gas sensing applications. The potential advantages of both the counterparts such as hardness, thermal stability, high refractive index and chemical stability of the inorganic material and easy synthesis, flexibility, low cost and lighter weight, environmental stability (e.g non-corrosive) [19] of the organic material can be exploited to achieve the desired outcome. New properties can emerge from the interaction of both the materials and can enhance their interfacial features. The addition of the inorganic component can significantly promote the sensing characteristics. Also, the symbiosis created between the parent polymer and the secondary component often delivers better performance than the bulk material alone [17].

Nanocomposite materials comprised of organic and inorganic elements have attracted enormous attention in developing gas sensing films in modern days due to their tailor-made characteristics, easy process ability, small device size, room temperature operability, low cost and low power consumption. However, sensors based on CPs possess some inherent shortcomings such as low sensor response, long response time, poor reproducibility and shorter life time [9].

CP based hybrid gas sensors with proper doping have exhibited encouraging results with improved optical, electrical, or mechanical properties. Such nanocomposite materials can develop small grain size, enhanced surface-to-volume ratio, porous structure and good stability suitable for gas sensing applications [28]-[33]. The interaction with the analyte gas causes changes in current, resistance (conductivity) or electrochemical properties into the reorganized polymer chain. These changes result from the increase or decrease in charge density due to polymer/analyte interaction [34].

The CP based hybrid material can have improved structural properties, morphology, surface-to-volume ratio, increased conductivity by doping (redox reaction or protonation) with a proper organic/inorganic acid. Doping also increase the no. of active sites in the sensing material for enhanced gas adsorption [20], [27], [35].

Metal nanoparticles can exhibit unique properties than their bulk material. Gold nanoparticles, for example, changes color and act as catalysts. These nanoparticles can behave as semiconductors and have lower melting temperature [36], [37]. Metal oxides show a varied range of electrical behavior of electrically insulating (MgO, Al_2O_3), wide-band semiconductors (TiO_2, Ta_2O_5, SnO_2, ZnO) to metal-like (V_2O_5, ReO_2, RuO_2). Some of the metal oxides have a no. of stable oxidation states [38]. Polymeric materials display structural defects that play crucial role in gas sensing. On addition of metal oxides to the pure polymer, oxidation states of the former can control the defects and chemisorption of the analyte gas [38]-[40].

Reducing the bulk surface area to nanometer or micrometer scale of the metal oxides can significantly influence the electronic and sensing properties of the nanocomposite. The nanostructured powder form of metal oxides consists of single/poly crystallites with minimum aggregation and porous network. The physical and chemical properties of the nanostructured metal oxides can be very much different from their bulk nature. The conductivity of nanotube arrays of TiO_2 was reported to be almost 9 orders higher than that of bulk TiO_2. The improved conductivity can be resulted from greater level of crystallinity and surface area, and defined stoichiometry. They reveal the possibility of increased stability associated with hopping conduction [38].

Wide band-gap semiconductors like TiO_2, Ta_2O_5, SnO_2, WO_3, ZnO have been employed in photocatalytic applications [41], direct random access memory [42] and gas sensing applications [43]-[45].

In the present study, tantalum pentoxide nanopowder (Ta_2O_5) was used and incorporated in the PANi nanocomposite to study the NO_2 gas sensing properties. The typical morphology of tantalum pentoxide (Ta_2O_5) nanopowder is found as spherical or globule shaped structures with particle size of typically 20-80 nanometers (nm) with specific surface area in the 10 - 50 m^2/g range. Ta_2O_5 thin film was identified to be quite appropriate for applications in high-density dynamic RAMs as well as metal-oxide-semiconductor FETs and transparent optical coatings due to its potential properties such as wide band-gap, high dielectric constant and high refractive index [46].

Gas sensors based on metal oxides have several disadvantages like high operating temperature (200^0C-400^0C) and high power consumption leading to shorter life time [47], [48], and poor selectivity and reproducibility [49]. In the above mentioned and many other works of gas sensing, the metal oxides are incorporated into the polymer matrix through various chemical routes to mitigate the inherent shortcomings of metal oxide based gas sensors and to achieve improved gas sensing results.

Bulakhe et al. [50] devised a LPG sensor based on Ppy/TiO_2 operating at room temperature. They obtained a maximum sensor response of 55% towards 1040 ppm of LPG. Relative humidity affected the performance of the sensor. Y. Li et al. [51] reported an ammonia sensor based on PANi/TiO_2 nanofibre that was able to detect the gas at a very low concentration of 25 ppb at room temperature and found superior over PANi nanofibre without TiO_2. K. Jian et al. [52] demonstrated a high performance PANi/SnO_2 based CO has sensor that achieved excellent sensor response at a low operating temperature ($<75^0$C). The advantages of a conductive thick film of PANi combined with the benefits of the metal oxide which provided a greater surface area are the contributing factors.

S. B. Kulkarni and his group [53] devised a flexible, hybrid PANi-WO_3 sensor for ammonia gas detection at room temperature which showed excellent selectivity with 121% sensor response towards 100 ppm gas. V. Kruefu and his co-workers [54] reported a poly (3-hexythiolphene) 1.00 mole% Au loaded ZnO nanoparticles based hybrid sensor for ammonia gas sensing. The device presented high sensor response, fast response time and high selectivity at room temperature. Guo et al. [55] fabricated a Pth/WO_3 based NO_2 gas sensor with high sensor response and good selectivity at a low temperature ($<90^0$C). Sonker et al. [56] worked on a PANi/ZnO thin film based NO_2 gas sensor that achieved high response of $\sim 6\times10^2$ towards 20 ppm of the gas and short response and recovery time. A. Roy et al. [44] devised a PANi-Ta_2O_5 nanocomposite based LPG sensor that achieved 83% of sensor response and good selectivity at room temperature.

The gas sensing behaviour of the CP hybrid nanocomposite based sensors can be further improved by doping the material with appropriate organic acids such as CSA (camphor sulphonic acid), pTSA (p-toluenesulphonic acid), DBSA (dodecyl benzene sulphonic acid). Doping can cause significant change in the material structure, morphology and increase charge carrier density and nos. of active sites for gas adsorption thus making the nanocomposite suitable for gas sensing [19], [57].

Mane et al. [58] fabricated a chemiresistive DBSA doped Ppy-WO_3 hybrid nanocomposite sensor which showed high selectivity, excellent reproducibility and high stability with 72% sensor response towards 100 ppm of NO_2 gas at room temperature. It was established that the uniformly dispersed DBSA into the nanocomposite matrix enhanced the gas detection properties. N. Karmakar and his co-workers [59] demonstrated silver-polypyrrole thin film NO_2 gas sensor doped with various percentages of (5-25%) of pTSA. A chemiresistive response of 68% towards 100 ppm of NO_2 gas was obtained with a response time of 148 sec. and a recovery time of 500 sec. The sensor kept stable for the first 15 days at room temperature. Navale et al. [60] reported that the CSA doped Ppy/∞-Fe_2O_3 based NO_2 gas sensor could exhibit better response, stability and faster recovery time than the undoped Ppy and Ppy/∞-Fe_2O_3 sensor. Raut et al. [61] fabricated a PANi/CdS H_2S gas sensor doped with various weight percentages of CSA. The CSA doped PANi/CdS nanohybrid sensor achieved a high sensor response of 75%, good selectivity and stability of 97.34% at room temperature. Chougule et al. [28] studied the effect of CSA doping on the physical and gas sensing behaviour of Ppy/ZnO hybrid sensor. They obtained high selectivity towards NO_2 gas with sensitivity of 80% towards 100 ppm gas, short response time and better stability.

1.6 PANi as a Conducting Polymer

Among the conducting polymers, PANi has attracted enormous research attention due to its inherently remarkable properties such as environmental stability, easy synthesis process and high electrical conductivity. In PANi, both single and double bonds contain a localized σ-bond forming a strong chemical bond. Also, each double bond includes a weaker localized π-bond. The π-bond between the first and second carbon atoms is moved to the position between the second and third carbon atoms. In turn, the π-bond between the third and fourth carbon moves to the next carbon atom, and so on. As a result, the electrons in the double bonds travel along the carbon chain. Thus, conjugation takes place, allows electron flow along the polymer backbone [21].

PANi is consisted of para-substituted aniline fragments linked in a “head-to-tail” configuration possessing better mechanical properties, higher degree of crystallinity and chemical stability than the other irregular polymers.

The PANi chain bears a ordered structure with regularly placed alternating phenyl rings and nitrogen-containing groups. This structure gives rise to polyconjugation which is a transport route of charge carriers. During the oxidation process (removal of electrons), charge carriers (polarons) are generated. The nitrogen atoms of PANi act as the oxidation sites. In the leucoemeraldine form of PANi (reduced form) the content of oxidised nitrogen atoms become zero to nearly one in pernigraniline form (fully oxidised form). The emearldine form of PANi is the intermediate form and is the most stable form, in which every second nitrogen atom is oxidised and the polymer chain comprises of equal nos. of oxidised and reduced units. On oxidation, positive polarons are created in the polymer chain [24]. The emeraldine salt form of PANi (PANi-ES) can directly be obtained by oxidative polymerization. The various oxidation states of PANi are illustrated in Fig. 1.8.

Each of the above three states can exist both in base and protonated H+ salt form. Only the protonated salt form of PANi is conductive. Protonation means interaction of the acids with the nitrogen containing polymer matrix. Depending on the oxidation state and degree of protonation, the conductivity, optical and magnetic properties, and color of PANi can change [24].

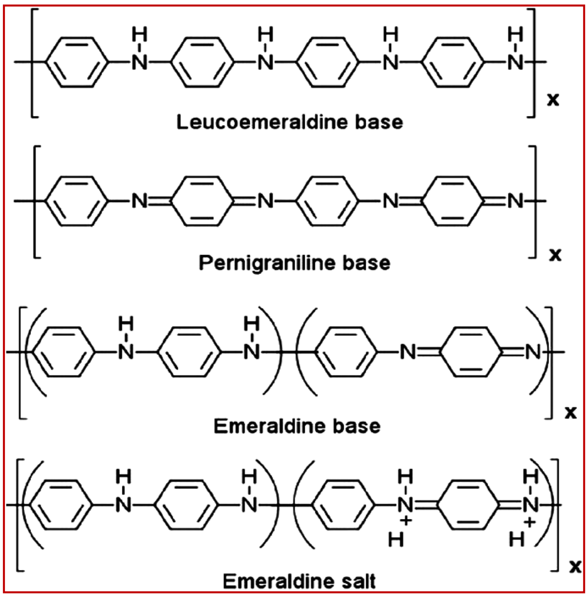

Fig.1.8. Oxidation states of PANi: a) leucoemeraldine base (fully reduced state), b) pernigraniline base (fully oxidised state), c) emeraldine base (half oxidised state- nonconductive), d) emeraldine salt (protonated form- conductive) [35].

Fig. 1.9 shows the chemical structure of one repeat unit of PANi in its emeraldine form. Each such unit is consisted of three benzene rings (numbered as 1, 2 and 3 in Fig.1.9) separated by amine (-NH) groups and one quinoid ring (numbered as 4 in Fig.1.9) surrounded by imine (-N=) groups [56]. The quinoid ring makes double bonds with nitrogen atoms with two pairs of carbon atoms in the ring and four π-electrons.

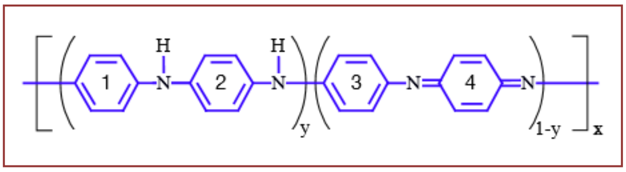

Fig.1.9. Chemical structure of PANi in emeraldine form (y=0.5 — y corresponds to the ratio of nitrogen atoms of amine type to the total nitrogen atoms in the repeat unit) [55].

1.6.1 The Doping effect on PANi

The CP molecules are covalently bonded and electrons are loosely bound. So, electron flow can be made possible. The process of doping enables these electrons to get detached from their respective π-bonds and roam around the polymer chain. The doping agents are the strong acids which stabilizes the polarons generated in the oxidation process. PANi shows both electronic and ionic conductivity. Under solid state, PANi in its emeraldine salt form shows conductivity ranging from 10^0 to 10^1 S/cm. Protonated emeraldine salt can have the charge carrier mobility from 10^{-3} to 10^{-1} cm^2/V-s [24]. Fig. 1.10 shows the protonation and deprotonation of PANi-emeraldine form.

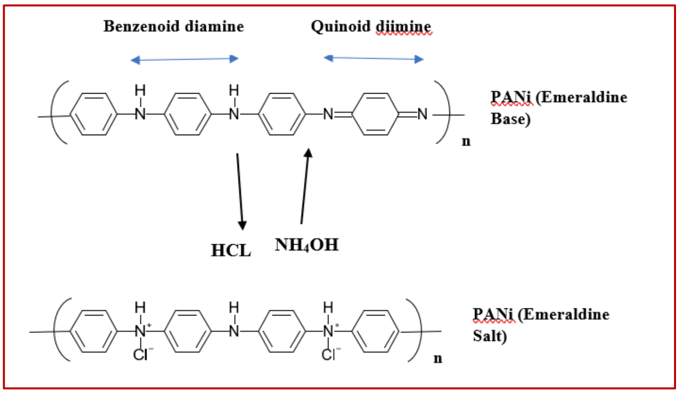

Fig.1.10. Protonation and deprotonation of PANi-Emeraldine form [62].

1.6.2 Use of PANi in gas sensing

Because of its low density and low toxicity, good environmental stability, easy synthesis, reversible doping-dedoping mechanism [63], flexibility and relatively good conductivity [64], [65], PANi has emerged as an excellent choice for the detection of various gases like NO_2, NH_3, CO, H_2S, H_2, ethanol, methanol [66]-[69], [30], [70]-[71] etc.. However, pure PANi based gas sensors suffer from some inherent drawbacks like weak selectivity, low reproducibility and stability, and slower recovery [10]. To alleviate these problems, PANi is often functionalized with inorganic metal oxide nanoparticles and acid doping to get the best sensing results. The addition of metal oxides into the PANi matrix improves not only the gas sensing properties, but also reduces the operating temperature [72].

In many of the past works, PANi is functionalized with wide-band semiconducting metal oxides such as TiO_2 [43], [50], [73], ZnO [35], [56], SnO_2 [45], [52], [71], WO_3 [53], [74], Ta_2O_5 [44], [75] for the detection of various environmentally toxic gases at a lower concentration level. In most of these works, sensing parameters were achieved at room temperature and found highly enhanced upon addition of the metal oxide. Fig. 1.11 depicts the various types of PANi based nanocomposites used for gas sensing [76].

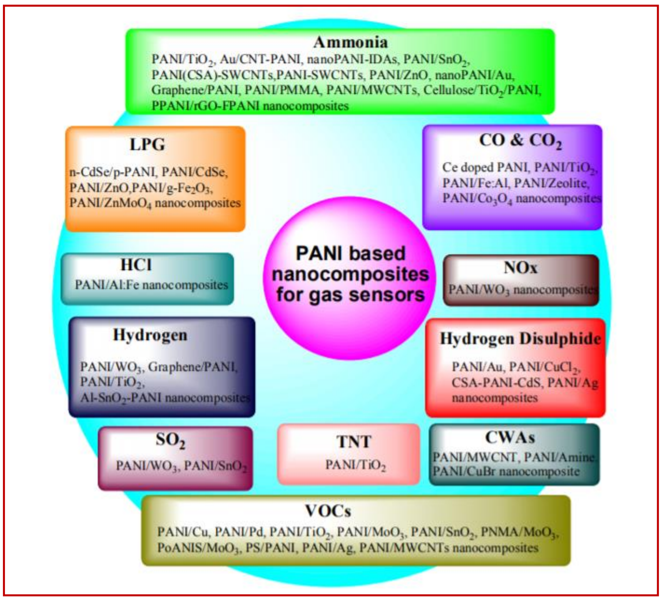

Fig. 1.11. Use of PANi based nanocomposite for gas sensing [76].

C. Zhu et al. [72] devised a $PANi/TiO_2$ nanocomposite ammonia gas sensor that exhibited good sensitivity and selectivity to 5.4 to 100 ppm and long-time stability at room temperature. Zoshki and co workers [35] fabricated PANi/ZnO thin film ammonia gas sensor with excellent sensor response.

Sharma et al. [45] demonstrated a $PANi/SnO_2$ based NO_2 gas sensor which operated at a low temperature and showed a high sensitivity of $\sim 3\times10^2$ towards 10 ppm of the gas and a faster response/recovery time. A. Kaushik et al. [74] reported a hybrid cross-linked $PANi/WO_3$ thin film sensor for NO_x gas sensing. The sensor operated at room temperature resulting in extended life-time and short response/recovery time of 30 sec. and 11 min. respectively. Sonker et al. [56] reported NO_2 gas sensor based on pure ZnO and PANi/ZnO thin films and came with encouraging results with PANi/ZnO compared to pure ZnO. A maximum response of $\sim 6.11\times10^2$ towards 20 ppm gas with a faster response and recovery time of about 2.16 min. and 3.5 min. respectively were obtained.

In many recent staudies, the gas sensing characteristics of the PANi/metal oxide based hybrid sensors were further improved by doping the nanocomposite material with organic acids such as CSA, pTSA, DBSA in various weight percentages [32], [58], [59], [61], [77]-[79]. Such kind of acid doping improves the solubility of the polymer by pervading the stiff backbone chain [80]. Doping also expedites gas adsorption mechanism of the sensing layer by increasing nos. of active sites.

1.7 Problem statement

Chemical sensors, more specifically gas sensors can provide a very effective solution in detecting the toxic gases even at trace levels. Metal-oxide-semiconductor (MOS) based gas sensors have been extensively researched in the gas sensing field owing to their high electron mobility, non-toxicity, high gas sensitivity and, chemical and thermal stability. But they usually operate at a high temperature ($>200^0$C) and hence lead to greater power consumption and shorter life-span [47], [48]. The MOS device circuit needs an additional heating component which needs careful monitoring and adds to extra cost. Moreover, weak selectivity of these devices is often reported because they can show simultaneous response to a large range of oxidizing and reducing gases. MOS based gas sensors are also influenced by atmospheric humidity [81]. These factors hinder the use of the sensors in practical applications.

Conducting polymer (CP) based gas sensors have been found to alleviate above stated problems and henceforth studied extensively in recent times. This category of sensors can operate at room temperature and can exhibit improved gas sensitivity and selectivity. The molecular structure of the sensing material can be easily modified by blending them with other organic/inorganic compounds to match with unique requirements of different applications. They are mechanically flexible and low cost devices, sustained with simplistic processing techniques. CP based nanostructures can possess a large surface-to-volume ratio and well-defined pore structures ideal for gas sensing [82].

The room temperature based gas sensors often succumb to adverse affects of surrounding humidity and thus can produce incorrect results. Therefore, it is important to undertake humidity study of these sensors.

In the current research work, it is proposed to devise two different configurations of PANi based hybrid nanocomposite sensors for detecting environmentally harmful NO_2 gas at lower concentration levels – i) the chemiresistive two-electrode based sensor and ii) the OFET based sensor utilizing CSA (Camphor Sulphonic Acid) doped PANi (Polyaniline)-Ta_2O_5 (Tantalum Pentoxide) nanocomposite.

Notable advantages of OFET based sensors over chemiresistive types have been established in the literature. OFETs can provide improved sensor response and selectivity, and above all, their intrinsic advantage to give access to important electrical characteristics such as charge carrier mobility (μ), threshold voltage (V_{TH}), on/off current ratio (I_{ON}/I_{OFF}), and sub threshold swing (SS). Fully characterized OFETs enable to extract more sensing parameters leading to improved gas sensing features. One distinguishing feature of OFETs is that the aforementioned electrical properties can exhibit conspicuous change under the influence of the analyte gas. Reliable, high-performance OFETs are achievable at low cost, and this can facilitate large-scale manufacturing. This opens the door for utilizing use-and-throw miniature, non-toxic, cost-effective sensors in industry and health sectors.

1.8 Objectives of the research

The primary objective of the present research work is to develop room temperature based organic electrical sensors for the detection of atmospheric pollutant NO_2 gas at a lower concentration level. The focus of the study is to implement low cost, small-sized, environment-friendly and high-performance CP based gas sensor device that can be used in industries, health sector and house-hold setups, where NO_2 gas detection and monitoring are of paramount importance. The current work is based on implementing the NO_2 gas sensing device in two platforms- i) thin-film chemiresistive type and ii) OFET based. The objectives of this work aim at realizing the following accomplishments.

- Synthesis of PANi in emeraldine salt form and PANi based hybrid nanocomposites, viz., PANi-Ta_2O_5 (50 wt%) doped with 20 wt%, 30 wt% and 40 wt% of CSA using chemical oxidative polymerization.
- Study of morphology, structure and spectroscopic nature of the aforesaid PANi samples, viz., pure PANi (emeraldine salt), PANi-Ta_2O_5, PANi-Ta_2O_5-CSA20%, PANi-Ta_2O_5-CSA30% and PANi-Ta_2O_5-CSA40%.

- Fabrication of chemiresistive sensors based on thin film utilizing the synthsized PANi nanocomposites and study of NO_2 gas sensing characteristics such as sensor response, reponse/recovery time, repeatability, selectivity, and study of the influence of relative humidity on the sensor performance.
- Fabrication of OFET based sensor utilizing PANi-Ta_2O_5-CSA40% as the sensing material. The work aims at investigating the electrical characteristics of the device such as charge carrier mobility (μ), threshold voltage (V_{TH}), the current ratio (I_{ON}/I_{OFF}), sub threshold swing (SS) and trap density.
- Study of NO_2 gas sensing behaviour of the OFET device fabricated.
- Investigation of the changes in the basic electrical parameters of the OFET designed and, its output and transfer characteristics upon exposure to different concentrations of NO_2.

1.9 Organization of the thesis

The major contribution of the thesis is towards fulfilling the design and development of a cost-effective, portable, room temperature operable CP based NO_2 gas sensor. This thesis is organized in five chapters and a bibliography. The literature survey is included in different sections of the chapters after each major study.

Chapter 1 presents the introduction part of the research work. The chapter unveils the toxic effects of NO_2 gas endangering environment and human lives. The chapter throws light in gas sensors, use of CPs and their hybrid incarnation in NO_2 gas sensing. Finally, it discusses the synthesis and properties of PANi - the primary material used in the design of the device under study. PANi, a contending CP, has been discussed in terms of its structure, doping effects and gas sensing behaviour.

Chapter 2 illustrates the experimental details of the synthesis process of the PANi nanocomposite and its material characterization studies. Results of in-depth spectroscopic and morphology experimentation of the PANi nanocomposites intermeshed with Ta_2O_5 and doped with CSA were diligently presented. The discussion digs into the potentiality of the synthesized PANi sample in gas sensing.

Chapter 3 demonstrates the experimental details of the fabrication process of the CSA doped PANi-Ta_2O_5 based chemiresistive thin-film sensor device. The NO_2 gas sensing properties of the device were investigated and the findings are studied. The favourability of the device as room-temeprature operable NO_2 gas sensor was discussed.

Chapter 4 furnishes the final major work of the research. It elaborates the fabrication aspects of the room temperature based OFET based NO_2 gas sensor utilizing the optimal performing CSA doped PANi nanocomposite and the conscientious investigation of its electrical characterization. The gas sensing properties of the sensor were examined and findings are elucidated.

Chapter 5 presents the concluding part of the research work. It highlights the advantageous and favorable use of OFETs utilizing the in-house synthesized PANi sample towards NO_2 gas sensing. It comments on the OFETs outperforming the chemiresistive counterpart. It endues in the challenges and shortcomings met with the device under investigation and the possible solutions. The chapter concludes the thesis work by citing upon the future scope of OFETs for better performance in the highly evolving field of gas sensing.

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