CHAPTER I

INTRODUCTION AND LITERATURE SURVEY
# CHAPTER I

## INTRODUCTION AND LITERATURE SURVEY

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Section – A: General Introduction

1.1 Introduction

1.1.1 Sensor and Types of Sensors

1.1.1.1 Sensor

According to Jacob Fraden in the Handbook of modern sensors [1], the definition of sensor is “a device that receives a signal or stimulus and responds with an electrical signal”. The reason for the output of a sensor to be limited to electrical signals is related to the present development of signal processing, that is almost exclusively performed using electronic devices. Referring this definition, a sensor should be a device that receives a physical, chemical or biological signal and converts it into an electric signal that should be compatible with electronic circuits. This definition may also be supported from the etymological origin of the word sensor. Sensor seems to be come from the word sense given that usually sensor devices try to mimic human senses characteristics. In the biological senses, the output is also an electrical signal that is transmitted to the nervous system. Another term with a meaning similar to sensor is transducer. Difference between transducer and sensor can be realised by the definition of transducer which is “transducer is any device which converts a stimulus into any other form, whether electric or not”. Usually sensors are part of larger complex systems, made by many other transducers, signal conditioners, signal processors, memory devices and actuators.

1.1.1.2 Types of sensors

In general, sensors can be classified into many types based upon the applications, input signal, conversion mechanism, material used in sensor, production technologies or sensor characteristics such as cost, accuracy or range.
**Table 1.1 Classification of sensors**

<table>
<thead>
<tr>
<th>Type</th>
<th>Detection Properties</th>
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<td>Thermal Sensor</td>
<td>Temperature, Specific heat, Heat flow, etc.</td>
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<tr>
<td>Electrical Sensor</td>
<td>Charge, Current, Voltage, Resistance, Inductance, etc.</td>
</tr>
<tr>
<td>Magnetic Sensor</td>
<td>Magnetic flux density, Magnetic moment, etc.</td>
</tr>
<tr>
<td>Optical Sensor</td>
<td>Light intensity, Wavelength, Polarization, etc.</td>
</tr>
<tr>
<td>Mechanical Sensor</td>
<td>Length, Acceleration, Flow, Force, Pressure, etc.</td>
</tr>
<tr>
<td>Chemical Sensor</td>
<td>Composition, Concentration, pH, etc.</td>
</tr>
</tbody>
</table>

The given classification of sensor is based upon the input signal to the sensor. Accordingly, the sensors can be classified into six different types, which are mentioned in the table 1.1. Thermal sensors are used to measure temperature, specific heat, heat flow or entropy. Electrical sensors are used to measure charge, current, voltage, resistance, inductance or capacitance. Magnetic sensors are used to measure magnetic field intensity, magnetic flux density, magnetic moment or magnetic permeability. Optical sensors, sometimes also called radiant sensors and are used to measure light properties, such as, intensity, phase, wavelength or polarization; or optical properties of a material, such as emissivity or reflectivity. Mechanical sensors are used to measure length, acceleration, flow, force, pressure or acoustic wave amplitude, etc. Finally, chemical sensors are the ones used to determine chemical properties of substances, such as the composition of a mixture, the concentration of a substance, the pH or the rate of a chemical reaction. Gas sensors are included in the chemical sensors class.

The sensor characteristics may be used to classify the sensors. This approach is frequently observed in catalogues or data sheets and is very useful when looking for sensors that meet specific demands. Having in mind the sensors applications, it may be noticed that sensors for outdoor use need to be less influenced by environmental conditions than those used indoors, where environmental factors usually changes little bit. Sensors used for continuous monitoring should have long term stability but may have lower resolution than a
sensor used for accurate, but timely spaced measurements. Sensors intended for domestic applications should be much cheaper than the ones used for military or scientific purposes. The fact that a sensor being developed shows lower sensitivity than previously studied ones and does not mean that it is not worthwhile to continue the research, since it might show characteristics other than sensitivity that may be advantageous in some application where a high sensitivity is not fundamental.

Finally, one must consider the materials and the technologies used to produce the sensors. These two classifications are important for development of engineers and research centers, since the knowledge on material production technology is a key issue in sensor development.

1.1.2 Need for Gas Sensors

Today’s society has brought numerous luxury items but with them series of problems like air pollution and emission of toxic gasses have also been introduced to our society. The necessity to constantly monitor and control the gases emitted sprouted the need for gas sensors. The various uses of gas sensors vary across a wide range from industrial to domestic applications; for example monitoring air pollution, chemical processes and exhaust from combustion engines. In recent years, several types of gases have been used in different areas of industries as raw materials. It becomes really important to control and monitor these gases, as there is a huge risk of damage to property and human lives if a leak occurs. Certain gases are corrosive, explosive or can be toxic for humans. There are currently three categories in which gas monitoring is needed:

- For oxygen (O₂), in connection with the monitoring of breathable atmospheres and for the control of combustion.

- For flammable gases in air in order to protect against the unwanted occurrences of fire or explosion. In this case concentrations to be measured are in the range up to the lower explosive limit, which for most gases, is up to a few percent.
• For toxic gases in air, where the need is to monitor concentrations around the exposure limits which range from less than 1 ppm to several hundreds of ppm.

Therefore, we need gas sensors that can detect these gases continuously and effectively to avoid most of the problems.

Over the past 20 years, a great deal of research effort has been directed toward the development of small dimensional gas sensing devices for practical applications ranging from toxic gas detection to manufacturing process monitoring. The increasing demand is for better gas sensors with higher sensitivity and greater selectivity. Intense efforts are being made to find more suitable materials with the required surface and bulk properties for the use as gas sensors. Among the gaseous species to be observed are nitric oxide (NO), nitrogen dioxide (NO₂), carbon monoxide (CO), carbon dioxide (CO₂), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), ozone (O₃), ammonia (NH₃), and organic gases such as methane (CH₄), propane (C₃H₈), liquid petroleum gas (LPG), and many others. Most important is once a gas sensor is developed to meet a strong demand from our society, a prosperous new market would be created.

1.1.3 Gas Sensors and Their Classification

1.1.3.1 Gas sensors

Gas sensors are devices that can change the concentration of an analyte gas into an electronic signal [2] and are an important component of devices commonly known as “electric noses” [3]. Instead of analyzing all of the individual gas constituents by techniques such as gas chromatography, optical spectroscopy, or mass spectrometry, gas sensors look for specific patterns or fingerprints of the response of different materials to the gas mixture. A gas sensor must possess at least two functions: to recognize a particular gas and conversion of output into measurable sensing signals. The gas recognition is carried out through the surface chemical processes due to gas–solid interactions. These interactions may be in the form of adsorption, or chemical reactions. The transducer function in gas sensor is dependent on the sensor material itself. The
transduction modes employed are due to the change of thermal, mass, electrical or optical properties. However, most gas sensors give an electrical output, measuring the change of current or resistance or capacitance.

1.1.3.2 Classification of Gas Sensors

The gas detection is based on the fact that changes in gases atmosphere alters the properties of the sensing layer in the characteristic way, which is transformed into signal by the transducer. The sensing layer is optimized by the proper choice of the material and the signal transfer component by a suitable technology. The gas sensors can be classified into different types based upon the changes in the properties of the sensing material. They can be classified into following types:

1) **Optical gas sensors** – In case of optical sensors, changes in the ambient atmosphere changes the optical properties of the sensor element. e.g. optical thickness or adsorption which are measured by interferometers, optical wave-guides, fibres etc. The sides or tips of the optic fibres (thickness, 2mm) are coated with a fluorescent dye encapsulated in a polymer matrix. Polarity alterations in the fluorescent dye, on interaction with the vapour, changes the dye’s optical properties such as intensity change, spectrum change, lifetime change or wavelength shift in fluorescence [4-5]. These optical changes are used as the response mechanism for odour detection. Polyaniline-coated optical sensors have been used to detect ammonia at concentrations as low as 1 ppm and the linear dynamic range was between 180 and 18,000 ppm [6].

2) **Capacitive gas sensors** – Capacitive sensors respond by capacitive changes of the material, which are mostly detected through low frequency AC measurements.

3) **Mass sensitive sensors** – In case of mass sensitive sensors, the composition of the gas atmosphere affects the mass and thus the oscillating frequency which is used as transducers (e.g. Quartz micro balances, surface acoustic wave sensor). Surface acoustic wave sensor (SAW) composed of a piezoelectric substrate with an input (transmitting) and output (receiving) interdigital transducer deposited on top of the substrate. The sensitive
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membrane is placed between the transducers and an AC signal is applied across the input transducer creating an acoustic two dimensional wave that propagates along the surface of the crystal at a depth of one wavelength at operating frequencies. The mass of the gas sensitive membrane of the SAW device is changed on interaction with a compatible analyte and causes the frequency of the wave to be altered. Polymer-coated SAW devices have quite low detection limits, e.g. tetrachloroethylene, trichloroethylene and methoxyflurane have been detected at concentrations as low as 0.7, 0.6 and 4 ppm, respectively [7].

4) **Conductance sensors** – Conductance sensors respond with the changes in resistance, which is normally determined by a 2- or 4-point probe resistance measurement. (e.g. Metal oxide sensors, conductive polymer sensor, ionic conductors) Conducting polymer composites, intrinsically conducting polymers and metal oxides are three types of conductance sensors. The sensing material is deposited over two parallel electrodes, which form the electrical connections through which the relative resistance change is measured.

- **Metal Oxide Gas Sensors** - Many researchers have shown that the exposed gas molecules alter the properties of the metal oxide gas sensors [8]. The change in the property depends upon many factors like the microstructure of the sensing material, inherent properties of the base materials, surface areas, surfactants, temperature, humidity etc. The principle on which metal oxide gas sensors works is the change in resistance at high temperature due to interaction of gas molecules. Lot of research work has been carried out in recent years [9-16] to optimize the parameters of known metal oxides as well as to discover new materials. Semiconductor gas sensors were originally commercialized in Japan employing tin oxide as the sensitive component [17].
5) **Electrochemical gas sensors** - Electrochemical sensors operate by reacting with the gas and producing an electrical signal proportional to the gas concentration. A typical electrochemical sensor consists of a sensing electrode (or working electrode) and a counter electrode separated by a thin layer of electrolyte. Gas that comes in contact with the sensor first passes through a small capillary-type opening and then diffuses through a hydrophobic barrier and eventually reaches the electrode surface. The gas that diffuses through the barrier reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism. These reactions are catalyzed by the electrode materials specifically developed for the gas of interest. With a resistor connected across the electrodes, a current proportional to the gas concentration flows between the anode and the cathode. The current can be measured to determine the gas concentration. Because a current is generated in the process, the electrochemical sensor is often described as an amperometric gas sensor.

6) **Catalytic Sensors**

Potentially explosive mixtures of methane or other flammable gases, with air can be monitored by means of a catalytically active solid-state sensor. The device, often referred to as the ‘pellistor’, is essentially a catalytic microcalorimeter. It consists of a catalytic surface constructed around a temperature sensor and a heater, which maintains the catalyst at a sufficiently high temperature to ensure rapid combustion of any flammable gas molecules present. However, these sensors suffered from several problems, including loss of sensitivity with time due to poisoning and burning out when exposed to high gas concentrations [18].

7) **Heterojunction gas sensors**

Heterojunction gas sensors are a recently invented type of solid state gas sensor that can overcome some of these limitations of metal oxide gas sensors [19] and show other desirable characteristics such as fast response and recovery, selectivity towards specific gases, good sensitivity etc. The junction width or potential barrier, which gets developed at the interface between two
semiconductors changes by the influence of gas molecules. Thus the presence of
the gas can be detected by heterojunction devices specially liquefied petroleum
gas (LPG), which is being widely used for domestic purpose. The region of
heterojunction is the interface between the two consisting semiconducting
materials, which behaves like a p-n junction. Gases adsorbed on either side of
the heterojunction are oxidised at varying rates at the heterojunction interface
and influence its barrier characteristics.

Heterojunctions have fast response time, cross selectivity, improved
sensitivity, reduced cost and important potential for miniaturization leading to
low power consumption.

1.1.4 Liquified Petroleum Gas (LPG)

LPG or LP Gas is the abbreviation of Liquified Petroleum Gas. Like all fossil
fuels, it is a non-renewable source of energy. The main components of LPG are
Propane ($C_3H_8$) and Butane ($C_4H_{10}$), which can be stored separately or as a
mixture. Depending upon the source of LPG and method of production of LPG,
it may contain components other than hydrocarbons. LPG is a gas at atmospheric
pressure and normal ambient temperatures, but it can be liquefied when
moderate pressure is applied or when temperature is sufficiently reduced. Due to
these properties, LPG can be easily condensed, packaged, stored and utilized,
which makes it an ideal energy source for a wide range of applications.

There are two main sources of LPG, namely:

1) Wet natural gas
2) Refinery operations

LPG prepared from wet natural gas consists entirely of “saturated”
hydrocarbons, i.e. propane and butane. LPG produced by both cracking and
reforming processes will have, in addition to saturated hydrocarbons, some
quantities of unsaturated hydrocarbons also (i.e. propylene and butylene). LPG
produced will have impurities like moisture & sulphur compounds like hydrogen
sulphide and mercaptans. Moisture may lead to clogging of regulators, valves
etc. and sulphur compounds cause corrosion. Moisture and sulphur compounds are, therefore removed by suitable treatment at the refinery.

1.1.4.1 Important properties of LPG

1. **Liquid Density** - LPG at atmospheric pressure and temperature is a gas, which is 1.5 to 2.0 times heavier than air. LPG readily liquefies under moderate pressures. The density of the liquid is approximately half that of water and ranges from 0.525 to 0.580 at 15°C.

2. **Vapour Pressure** - The vapour of LPG in equilibrium with its liquid exerts a pressure called the vapour pressure and the magnitude of this pressure is dependent on the ambient temperature and not on the quantity of the contents. Vapour pressure increases rapidly with temperature. The vapour pressure of LPG should be nearly equal to 8 Kg/sq.cm.

3. **Explosive Limits** - LPG has an explosive range of 1.8% to 9.5% volume of gas in air. This is considerably narrower than other common gaseous fuels. This gives an indication of hazard of LPG vapour accumulated in low-lying area in the eventuality of the leakage or spillage.

4. **Odour** - LPG has only a very faint smell and consequently it is necessary to add some odourant, so that any escaping gas can easily be detected. Ethyl Mercaptan is normally used as stenching agent for this purpose. The amount to be added should be sufficient to allow detection in atmosphere 1/5 of lower limit of flammability.

5. **Colour** - LPG is colourless both in liquid and vapour phase. During leakage the vapourisation of liquid cools the atmosphere and condenses the water vapour contained in them to form a whitish fog which may make it possible to see an escape of LPG.

6. **Toxicity** - LPG even though slightly toxic, is not poisonous in vapour phase, but can, however, suffocate when in large concentrations due to the fact that it displaces oxygen. In view of this the vapour possesses mild anaesthetic properties.
LPG is widely used in the food industry for domestic (cooking) purpose. It can be used in glass and ceramic industry as fuel like LPG can enhances the product quality thereby reducing the technical problems in manufacturing. LPG is used in metal industries basically for cutting, heating and melting processes also in agro industries for horticultural, agricultural, heating and drying processes. LPG can be used as an automotive fuel or as a propellant for aerosols, in addition to other specialist applications. Because of the advantages of LPG over other fuels, it is being used for many applications.

The advantages of LPG is as follows

1.1.4.2 Advantages of LPG

(i) **Energy Efficient:** LPG’s energy density (calorific value per unit mass) is higher than conventional fuels and there are no residues and un-burnt products of combustion making it a compact and energy efficient fuel.

(ii) **Cost effective:** LPG is cost-effective compared to electricity, diesel and petrol. It gives you savings in fuel bills as well as other associated costs.

(iii) **Clean & Environment friendly:** LPG gives a clean blue flame. This is because it does not produce harmful emissions like soot, smoke, un-burnt carbon particles and other obnoxious gases.

(iv) **High Portability:** Both Propane and Butane are easily liquified and stored in pressure containers. These properties make the fuel highly portable and hence, can be easily transported in cylinders or tanks to end-users.

(v) **No contamination:** LPG or its products of combustion do not contaminate product ensuring that product is hygienic and of superior quality.

(vi) **Reliability:** LPG contains no lead resulting in a much cleaner fuel. It is non-poisonous and safe to use.

The clean burning properties and portability of LPG provide a substitute for traditional fuels such as wood, coal and other organic matter. This provides a solution to de-forestation and the reduction of particulate matter in the atmosphere (haze), caused by burning the traditional fuels.
Section – B: Literature Survey

In recent years, semiconductor materials have attracted great attention from chemists, physicists and materials scientists due to their unique and special chemical, physical and mechanical properties. Therefore, increasing attention is being paid to studies on less known chemical compounds able to act as semiconductors to meet the need of the future technology. In this study, lead sulfide (PbS), two conducting polymers named polyaniline and polypyrrole have been studied separately and after fabricating heterojunction between polyaniline/PbS and polyaniline/polyprrole are used for room temperature LPG sensor.

1.2 Lead Sulphide Thin Film

Most studied semiconductors belong to the II-VI and IV-VI groups of periodic table as they are relatively easy to synthesize and are generally prepared as particles or in thin film form. Lead sulfide (PbS) is an important binary IV–VI semiconductor material with a rather narrow band gap (0.41 eV) at room temperature and a large exciton Bohr radius (18 nm). The band gap can be blue shifted from the near infrared (IR) to the visible region by forming nanocrystallites [20]. Consequently, PbS nanoparticles have exhibited novel and excellent optical and electrical properties and applications in nonlinear optical devices such as IR detectors [21]. The advantages of these nanostructured films are regarding to the size of the semiconductor bandgap, which can be controlled by adjusting the size of the nanoparticles by adding oxidant agents during deposition [22]. Lead sulphide thin films have been utilized as photoresistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings [23, 24]. Physical properties of the thin films vary with the deposition method as well as the preparative parameters. Significant changes in the physical properties of pure PbS thin films were found with increase in the doping concentration by several workers [25–27]. PbS thin films can be prepared by almost all the physical and chemical methods. Kumar et al [28] have deposited the high quality polycrystalline thin films of PbS onto ultra-clean glass.
substrates by vacuum evaporation technique. Maheshwar et al [29] electrodeposited polycrystalline thin films of lead sulphide on titanium, aluminium and stainless steel (SS) substrates at a constant potential of −0.7 V vs. Ag | AgCl |(sat)KCl electrode. Effect of cationic precursor pH on optical and transport properties of successive ionic layer adsorption and reaction (SILAR) deposited nano crystalline PbS thin films has been studied by Preetha et al [30]. PbS nanocrystal solar cells with high efficiency and fill factor has been fabricated by Szendrei et al [31] showing power conversion efficiencies approaching 4% and fill factor of 60% under AM 1.5 illumination using spin coating technique. Chemical bath deposition (CBD) is one of the standard methods used for preparing PbS films. This method is less expensive, easy to handle, allowing deposition of films on a large area and on various substrates [32]. Because of these advantages, we have used CBD method for the deposition of PbS thin films. Many researcher have deposited PbS thin film using CBD method and used as-deposited and annealed PbS thin films for different applications. Raniero et al [33] deposited PbS thin films by CBD method and studied the response in the infrared region as well as its structure, surface morphology and electrical transport properties. The structural parameters like lattice constant, crystallite size, internal stress and strain of PbS thin films deposited by CBD method were studied by Choudhury and Sarma [34]. Diwaker et al [35] have synthesized PbS nanocrystallites and reported the optical band gap 2.0 ± 0.1 eV, which is higher than the bulk due to quantum confinement in PbS nanocrystallites. The growth parameters and thermal treatment influenced the structure, morphology and the optical properties of PbS thin films [36]. Popa et al [37] deposited PbS thin films by CBD method and demonstrated that the size of the PbS thin film crystallites affects the photoelectric properties of the material. PbS thin films can be employed individually for the detection of toxic gases like NH₃ or NO₂ in air. The room temperature response of PbS thin film towards these toxic gases has been reported by Tiexiang [38]. Markov and Maskaeva [39] reported that PbS thin film can be used as a sensing element for nitrogen oxide. The hydrogen sulfide chemisorption on PbS at 22–100 °C is
studied by static testing in a vacuum and by pulsed chromatography by Derlyukova et al [40]. From this literature survey it is clear that PbS thin film can be used to trace out toxic and flammable gases.

1.3. Polyaniline Thin Films

In 1971, the first intrinsic conducting polymer named polyacetylene was reported by Shirakawa et al. [41]. Conductive polymers such as polyaniline, polypyrrole, polyacetylene, polythiophene etc. continue to be the focus of active research in diverse fields including electronics, energy storage catalysis, chemical sensing and biochemistry. The concept of conductivity and electroactivity was quickly broadened from polyacetylene to other conducting polymers by Diaz et al. [42]. Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical and optical properties as well as good stability [43, 44], light emitting electrochemical cells [45], photodiodes [46], photovoltaic cells [47], field effect transistors [48], optocouplers [49], optically pumped lasers in solution [50] and solid state electrically pumped polymer lasers [51]. As a new class of microporous framework materials, conjugated microporous polymers have recently received much more attention [52]. Conjugated polymers have band gaps in the range of 1 to 4 eV, allowing stable optical excitations and mobile charge carriers.

The first report on the production of “aniline black” dated back to 1862 when Letheby [53] obtained a dark-green precipitate with a platinum electrode during the anodic oxidation of aniline in a solution containing sulphuric acid. This green powdery material soon became known as ‘aniline black’. The interest in this material retained almost academic for more than a century since “aniline black” was a powdering, intractable material, a mixture of several products which is quite difficult to investigate. Green and Woodhead performed the first organic synthesis and classification of intermediate products in the “aniline black” formation and three different aniline octamers were identified and named as leucoemeraldine, pernigraniline and emeraldine base. These names are still used, indicating various oxidation states of polyaniline (Fig. 1.1).
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Figure 1.1 Various states of oxidation and protonation of polyaniline.

Polyaniline is a typical phenylene-based polymer having a chemically flexible \(-\text{NH}\) group in a polymer chain flanked either side by a phenylene ring. It is a unique polymer because it can exist in a variety of structures depending on the value of \((1-y)\) in the general formula of the polymer shown in Figure 1.1 (a) [54, 55]. The electronic properties of polyaniline can be reversibly controlled by protonation as well as by redox doping. Therefore, polyaniline could be visualized as a mixed oxidation state polymer composed of reduced \{\(-\text{NH}\text{--B--NH--}\}\) and oxidized \{\(-\text{N=Q=N--}\}\) repeat units where \(-\text{B--}\) and \(=\text{Q=}\) denote a benzenoid and a quinoid unit, respectively forming the polymer chain (Figure 1.1 (a)), the average oxidation state is given by \(1-y\). Depending upon the oxidation state of nitrogen atoms which exist as amine or imine configuration, polyaniline can adopt various structures in several oxidation states, ranging from the completely reduced leucoemeraldine base state (LEB) (Figure1.1 (b)), \(y-1 = 0\), to the fully oxidized pernigraniline base state (PNB) (Figure 1.1 (c)), where \(1-y = 1\). The “half” oxidized \((1-y = 0.5)\) emeraldine base state (EB) (Figure1.1 (d)) is a semiconductor and is composed of an alternating sequence of two benzenoid units and a quinoid unit. The protonated form is the conducting emeraldine salt (ES). The electronic structure and excitations of these three insulating forms (LEB, PNB, EB) are contrasted. However, the LEB form can be p-doped
(oxidatively doped), the EB form can be protonic acid doped and the PNB form can be n-doped (reductively doped) to form conducting ES systems. The EB, intermediate forms of polyaniline can be non-redox when doped with acids to yield the conductive emeraldine salt state of polyaniline as demonstrated in Figure 1.2. It can be rendered conductive by protonating (proton doping) the imine nitrogen, formally creating radical cations on these sites. This doping introduces a counterion (e.g. Cl\(^-\), if HCl was used as the dopant) and recently, the counterion was affixed to the parent polymer by partially sulfonating the benzene rings in the polymer, resulting in a so-called “self-doped” polymer. Both organic acids such as HCSA (camphor sulfonic acid) and inorganic acids, such as HCl, are effective, with the organic sulfonic acids leading to solubility in a wide variety of organic solvents, such as chloroform and m-cresol. The protonic acid may also be covalently bound to the 16 polyaniline backbone, as has been achieved in the water-soluble sulfonated polyaniline (Figure 1.2). Similar electronic behavior has been observed for the other non degenerate polymers. Polyaniline is unique among intrinsically conducting polymers in that it can be doped with a proton donor, usually by adding an organic acid. This “protonic acid doping” gives a positive charge to the structure and results in a manyfold increase in the conductivity of polyaniline compared with the undoped form. Polyaniline is stable in air and its electronic properties are readily customized [56-60]. Each oxidation state has a specific colour and specific electrical properties. The interest in polyaniline-based junction devices is because of the processing ease and stability of polyaniline and the extensive knowledge base existing for this material. Conducting polyaniline has been used as sensing material for different vapors like methanol, ethanol, acetone and benzene and for various gases like NH\(_3\) and hydrogen [61, 62].
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Figure 1.2 Protonic acid doping of polyaniline (emeraldine base) to polyaniline (emeraldine salt).

Electrochemically polyaniline can be synthesized either by potentiostatic, galvanostatic or cyclic voltammetric techniques [63]. Films deposited potentiostatically and galvanostatically produces uniform deposition but not with less adherency. On the other hand, electro-oxidation of aniline by continuous cycling between the predetermined potentials produces an even polymeric film which adheres strongly to the electrode surface [64]. Polyaniline can be prepared in several oxidation states, with electrical conductivity varying progressively from $10^{-11}$ to 10 S/m or more.

Many reports are available on different modes of electrodeposition for polyaniline thin films. The polyaniline thin film electrode have been synthesized on graphite electrodes from hydrochloric acid solution under galvanostatic conditions [65]. Zhou et al [66] used pulse galvanostatic method to synthesize polyaniline (PANI) in HNO$_3$ solution and studied relationship between preparation conditions, morphology and electrochemical properties of polyaniline. Jiang et al [67] studied one-dimensional growth and electrochemical properties of polyaniline deposited by a pulse potentiostatic method. $\gamma$-MnO$_2$ nanoparticles-coated polyaniline (PANI) nanofibers on carbon electrode were prepared by potentiodynamic electrochemical deposition of PANI and MnO$_2$ from a single pot have been prepared by Surya Prakash et al [68]. Buron et al
Polypyrrole Thin Films

Pyrrole was known to form a conductive “pyrrole black” [78] via spontaneous polymerization and its history can be dated back in 1916 [79]. In 1968 [80], it was noted that pyrrole could be electrochemically polymerized using a variety of oxidation agents to give a black conducting powder. It can be synthesized in both aqueous and non-aqueous solutions during electrochemical polymerization. Among all known conducting polymers, polypyrrole (Ppy) stands out as an excellent one because of its good environmental stability, high conductivity, and ease of preparation. Polypyrrole is electroactive polymer which experiences a change in shape and size in response to electrical stimulation. The electroactive polymers are classified into two types electrical...
and ionic electroactive polymers. Polypyrrole is ionic electroactive polymer as the anions are entering and existing the polymer matrix in the presence of potential difference. The changes in volume are due to electrochemical oxidation and reduction of polymers in presence of anions in the electrolyte [81-82]. In contrast to polyaniline it can operate both in acidic and neutral solutions, which makes polypyrrole electrode attractive for use as sensors material and also the oxidation potential of polypyrrole is low. For all of these reasons, polypyrrole has been an interesting material to study. The structure and the properties of polypyrrole are strongly influenced by the number of parameters such as oxidation potential, the monomer concentration, temperature etc. The polypyrrole can be synthesized by variety of methods. Polypyrrole can be prepared by chemical oxidation process with different oxidizing agents. Polypyrrole nanowire arrays were synthesized by Hassanzadeh [83] through chemical polymerization inside the nanochannels of alumina membrane. Jeon et al [84] chemically synthesized ultra-thin polypyrrole nanosheets for chemical sensor application. The electrochemical synthesis of polypyrrole can be conveniently carried out. An advantage of the electrochemical methods is that the preparation process can be simply controlled through the current or the applied potential and the charge consumed. Various reports are available on electrochemical synthesis of polypyrrole [85-88]. In the last few years, the goal of researchers is to improve physical properties of polypyrrole- like processibility and mechanical integrity. To achieve this goal, composites and copolymers of polypyrrole were synthesized. [89-91]. Polypyrrole can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer. The formation of polypyrrole from a monomer of pyrrole is as shown in Figure 1.3
Fig. 1.3 Formation of polypyrrole from pyrrole monomer [81]

In recent years conducting polymers like polypyrrole and polyaniline have been studied as sensing materials essentially due to their operation at room temperature and easy sensor element processing [92-93]. Recently, Qin et al [94] demonstrated a fiber optic reflectance sensor using Polypyrrole conducting polymer to detect volatile organic compounds (VOCs). Joshi et al [95] studied ammonia sensing properties of polypyrrole thin films at room temperature. Chemically polymerised polypyrrole composite thin film has been reported by Sun et al [96] as highly sensitive humidity sensor. Toxic nitrogen dioxide sensing capability of polypyrrole was tested by Paul et al [97]. Influence of electrodeposition parameters on polypyrrole based ammonia gas sensor has been studied by Patois et al [98]. Pirsa et al [99] reported gas sensor based on nanostructure conductive polypyrrole for determination of volatile organic
solvents. Su et al [100] reported a novel flexible \( \text{H}_2 \) gas sensor by the layer-by-layer self-assembly of a polypyrrole thin film on a polyester substrate. Other than gas sensor application, the polypyrrole thin films have been used to study the supercapacitive behaviour. Dubal et al [101, 102] reported the specific capacitance values 533 and 476 \( \text{Fg}^{-1} \) for polypyrrole thin films deposited by SILAR and electrodeposition methods, respectively.

### 1.5 Heterojunction Gas Sensor

A semiconductor heterojunction is the interface formed between two dissimilar materials having different bandgaps. The interface formed shows the characteristic similar to the p-n junction diode. Current flows easily in forward biased with negligible resistance and small amount of current flows in reverse biased. William Shockley et al [101] explained the basic theory of current-voltage characteristics of heterojunction. Heterojunctions have been receiving attention for considerably long time because of their several useful applications as switching devices, solar cells and ultraviolet photodetectors [102]. Literature survey of heterojunction during last few years revealed that, mostly heterojunctions were fabricated for photovoltaic applications. The use of heterojunction as gas sensors was first proposed by Nakamura et al. in 1986 [103]. The sensor was simply made by mechanically contacting a p-type \( \text{CuO} \) ceramic and an n-type \( \text{ZnO} \) ceramic pellet. The hetero contact showed a high sensitivity and selectivity to \( \text{CO} \) gas over \( \text{H}_2 \). The working mechanism suggested by Nakamura et al was that the adsorbed molecules of reducing gases form interface states that can change the potential barrier height and consequently the current across the junction.

Heterojunction between two semiconductors are fabricated by different physical and chemical methods. Recently, Rao et al [104] have fabricated p-ZnTe/n-CdTe heterojunction diodes by vacuum deposition technique. Reddy et al [105] studied SnS/ZnMgO heterojunction formed by RF sputtering technique. Aksoy et al [106] fabricated nanostructure n-ZnO/p-Si heterojunction diode by sol–gel method. Choi et al [107] fabricated p-Si nanowire/ZnO film.
heterojunction by electroless wet chemical etching process and RF magnetron sputtering at room temperature respectively. The gas responses of several heterojunction sensor systems to target gases including CO, H₂, H₂O, NO₂ and C₃H₅OH have been investigated [108-113]. Ling et al [114] have studied the NO₂ and CO₂ sensing properties of a heterojunction gas sensor formed between n-type ZnO and a p-type composite based on a mixture of BaTiO₃/CuO/La₂O₃ and compared with the performance of its component p- and n-type materials. It was found that the individual ZnO and BaTiO₃/CuO/La₂O₃ sensors showed resistance increase when exposed to NO₂. The resistance also decreased when exposed to low levels of NO₂, indicating that a different detection mechanism was operative at the heterocontact compared with the single-phase materials. The sensing properties of CuO/ZnO heterojunction gas sensors have been studied by Hu et al [115] for H₂S and alcohol vapors which is operated at 381 K.

Many reports are available on heterojunctions based on metal chalcogenides for specially photovoltaic application. Ghosh et al [116] fabricated heterojunction between SnS/CdS for photovoltaic application. Ichimura et al [117] studied CdS/SnS heterojunction and calculated the energy band offset at the CdS/SnS heterojunction using density-functional, pseudopotential method. Electrical properties of doped polypyrrole/silicon heterojunction diodes and their response to NOₓ gas have been studied by Tuyen et al [118]. Along with this polyaniline–titanium dioxide nanocomposite thin film gas sensor have fabricated by Tai et al [119] for NH₃ and CO sensing and reported that the resistance of film increases as soon gas is exposed. Polymer based heterojunction are also being used for the detection of widely used liquefied petroleum gas at lower concentrations. Detection of LPG at lower concentrations can avoid big explosions. Following table describes the different heterojunctions reported as LPG sensors.
### Table 1.1 Different heterojunctions for LPG detection.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sensor</th>
<th>Author</th>
<th>Sensitivity &amp; Gas Concentration</th>
<th>Response time (s)</th>
<th>Recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-CdTe/p-polyaniline</td>
<td>Joshi et al [120]</td>
<td>67 % at 0.14 Vol%</td>
<td>80-300</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>n-CdSe/p-polyaniline</td>
<td>Joshi et al [121]</td>
<td>70 % at 0.08 Vol%</td>
<td>50-100</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>n-CdS/p-polyaniline</td>
<td>Dhawale et al [122]</td>
<td>80 % at 0.08 Vol%</td>
<td>105</td>
<td>165</td>
</tr>
<tr>
<td>4</td>
<td>p-polyaniline/n-TiO₂</td>
<td>Dhawale et al [123]</td>
<td>63 % at 0.1 Vol%</td>
<td>140</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>p-polyaniline/n-ZnO</td>
<td>Dhawale et al [127]</td>
<td>81 % at 0.1 Vol%</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>6</td>
<td>n-Bi₂S₃/p-CuSCN</td>
<td>Ladhe et al [124]</td>
<td>70 % at 0.1 Vol%</td>
<td>158</td>
<td>158</td>
</tr>
<tr>
<td>7</td>
<td>p-PEDOT:PSS/n-ZnO</td>
<td>Ladhe et al [125]</td>
<td>59% at 0.08 Vol%</td>
<td>225</td>
<td>190</td>
</tr>
<tr>
<td>8</td>
<td>p-polyaniline/n-PbS</td>
<td>Patil et al [126]</td>
<td>70% at 0.06 Vol%</td>
<td>125</td>
<td>200</td>
</tr>
<tr>
<td>9</td>
<td>p-polyaniline/n-polypyrrole</td>
<td>Patil et al [127]</td>
<td>33 % at 0.08 Vol%</td>
<td>154</td>
<td>161</td>
</tr>
</tbody>
</table>

### 1.6 Orientation and Purpose of the Dissertation

Liquified petroleum gas (LPG) is often used as a fuel source. LPG includes propane, propylene, butane and butylene. LPG is used in domestic, commercial, agricultural and industrial settings. It is highly explosive when it accumulates in one area. Even at low concentrations of LPG, serious problems may occur due to its flammable characteristics. LPG can form explosive mixtures with air. Since the gas is slightly heavier than air, it may form a continuous stream that stretches a considerable distance from a leak or open container, which may lead to a flashback explosion upon contacting a source of ignition. The widespread use of LPG in food industry, metal industry, aerosol industry, automotive industry, textile industry and as fuel for automobile vehicles require detection of LPG to measure the leakage of gas in order to avoid accidental explosions.

Commercially, available option is metal oxide based gas sensor devices. These sensors have several unique advantages such as low cost, small size, measurement simplicity, durability, ease of fabrication and low detection limits (< ppm levels), but suffer from low selectivity to specific target gases and high operation temperature and lower sensitivity. Thus, increase in power...
consumption, reduce sensor life, limit the portability, etc. Though metal oxides have been extensively used for gas sensor, a new approach is needed to increase this selectivity and sensitivity at room temperature (300K). The development of gas sensors to monitor the combustible gases is essential due to the concern for safety requirements in the homes and for the industry. As an option, there is a scope to fabricate heterojunctions between organic and inorganic materials with enhancement of the sensor characteristics and mechanical strength. This will be done by fabricating heterojunctions between p-polyaniline/n-PbS and p-polyaniline/n-polypyrrole with a high rectifying ratio by adopting chemical routes and used for LPG sensor by considering potential barrier height, which gets changed at the interface of heterojunction upon exposure of gas molecules.

The objective of present work is to search innovative low-cost chemical methods for the detection of LPG at room temperature by fabrication of heterojunction between polyaniline/PbS and polyaniline/polypyrrole. These chemical methods are cost effective. Chemical methods of thin film deposition are easy and economical. In these methods, it is not necessary to have very pure starting materials.

Lead sulfide (PbS) thin films will be deposited on a stainless steel substrate by chemical bath deposition (CBD) followed by polyaniline thin film by an electrodeposition (ED) method. Second heterojunction is organic heterojunction, which is in between polyaniline and polypyrrole. Both these polymers will be deposited by simple and inexpensive electrodeposition method. The structural, surface morphological, optical and electrical characterization of these films will be carried out prior to the fabrication of heterojunction. The X-ray diffraction (XRD) technique will be used for the structure identification. The surface morphology of the films will be studied using scanning electron microscopy (SEM). The optical properties will be studied in the visible range of spectrum using optical spectrophotometer. The electrical properties will be studied by dc two-point probe method. Surface wettability of these films will be studied using contact angle meter. The type of conductivity of these films will be studied using thermoelectric power measurement.
The current - voltage (I-V) characteristics will be studied in order to evaluate various electrical parameters to test the diode quality. The sensing performance at different concentrations of LPG will be studied at room temperature (300 K) by current-voltage (I-V) characteristics under the forward bias condition.

Lastly, the performance of LPG sensors will be evaluated in terms of their selectivity, sensitivity and stability. The selectivity of these heterojunction thin films will be calculated in presence of other gases in terms of selectivity coefficient. The LPG sensor performance of polyaniline/PbS and polyaniline/polypyrrole heterojunctions will be compared in terms of their gas response.
References

1777.


865.