Bhusaval Arts, Science and P.O.Nahata Commerce College,

Bhusaval - 425201

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Final Report of the Work Done on the

Minor Research Project

Entitled,

"Synthesis of Poly-Aniline Thin Film for the Gas Sensing Application"

Submitted to,

University Grants Commission, New Delhi.

By

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1.1 History of Conducting Polymer

A 'Polymer' is a chain of linked repetitive units "poly," many, and "mer," means unit or molecule. The organization and the components of the units create the many different types of polymers in the world. A model of a very simplistic polymer is, **-A-A-A-A-A-A-.**

Where "A" is the unit and each "A" is linked to another, "A" making it many units together. The way the individual "A," are linked is called a chemical bond. Bonds hold together atoms making up a molecule with the electrons from the atoms acting as the "glue." Chemical bonds are represented as lines between individual atoms. The number of chemical bonds that each atom can make is determined by the atom itself and varies from one type of atom to another [1].

Discovery of polymers has given a new dimension to the present era. Polymers are known so far as a class of heat sensitive, flexible, electrically insulating and amorphous materials. Electrically Conducting Polymers appear to be an ideal candidate for various applications. As many of their properties circumvent problems prevalent including corrosion, weight, matrix incompatibility, and environmental integrity [2]. In addition to being corrosion resistant and light weight, many critical properties of conducting polymers may be tailored for various applications. The strength to weight, possibility, resistance to corrosion, has given conducting polymers advantage over metals. Polymers are generally known for their insulating property because of covalent bond present in saturated carbon compounds. Since desirable properties can be conveniently attained by tailoring the polymer structure and also by incorporating additives; scientists have been enthusiastic to explore the possibility of transforming insulating polymers into conducting or semiconducting materials envisaging such special characteristics like low density, ease of fabrication, flexibility of design, low energy and labour requirements for fabrication and processing.

Conducting polymers were first discovered in 1976. In the mid 1970s, the first polymer capable of conducting electricity, polyacetylene, was reportedly prepared by accident by H.Shirakawa [3]. The subsequent discovery by **Alan Heeger and Alan MacDiarmid** that, polymer would undergo an increase in conductivity of 12 orders of magnitude by oxidative doping quickly reverberated around the polymer and electrochemistry communities and an intensive search for other conducting polymers soon followed [4].

In 1976, Alan MacDiarmid, Hideki Shirakawa, and Alan Heeger, along with a group of young students found that conductivity of polyacetylene increased by up to 6 orders of magnitude when reacted with iodine (from 10^{-4} S/cm to 10^{2} S/cm),this phenomenon, known as doping, as a result of charge carriers. In addition, it was

discovered that varying the level of doping yielded polymers exhibiting wide range of electrical properties, from insulator, or semi-conductor, to metal [5].

Since 1976, a number of conducting polymers, namely polypyrrole, polythiophene, and polyaniline, have become the focus of much study. The importance of conducting polymers is exemplified by the awarding of the **2000 Nobel Prize in Chemistry** to **MacDiarmid, Shirakawa, and Heeger,** for the discovery and the development of conducting polymers. This was particularly exciting because it created a new field of research and a number of opportunities on the boundary between condensed-matter physics and chemistry. As the commonly known polymers in general are saturated and so insulators, these were viewed as unexciting from the point of view of electronic materials. Conducting polymers are polymers containing an extended pi (π) conjugated system, made up of overlap of singly occupied p orbitals in the backbone of the polymer chain. Although conducting polymers possess a relatively large number of delocalized pi electrons, a fairly large energy gap exists between the valence band and the conducting band (greater than 1 eV), thus these polymers are considered to be semi-conducting, at best. These polymers must be doped (usually meaning altering the number of pi electrons) in order to order to render the polymers truly conducting. In conjugated polymers the electronic configuration is fundamentally different, where; the chemical bonding leads to one unpaired electron (the electron) per carbon atom. Moreover, bonding, in which the carbon orbitals are in the sp^2pz configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer. This electronic delocalization provides the highway for charge mobility along the backbone of polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry, i.e. the number and kind of atoms within the repeating unit, with the result that such polymers can exhibit semiconducting or even metallic properties
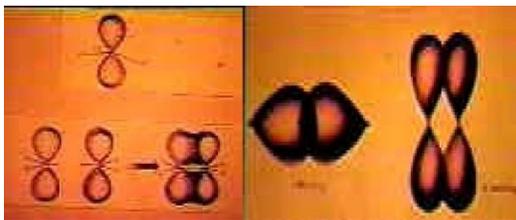

Figure 1.1
Pi (π) and Sigma (σ) bonding

Electrically conducting polymers are designated as the fourth generation of polymeric materials. Electronically conducting polymers are extensively conjugated in nature and therefore it is believed that they possess a spatially delocalized band-like electronic structure. These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner significant of the band structure

of solid-state semiconductors. It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework. The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the polymer respectively. The following figure shows the formation of molecular orbitals. The simplest possible form of conducting polymer is of course the arche type polyacetylene (CH) x. Polyacetylene it is too unstable to be of any practical value, its structure constitutes the core of all conjugated polymers [6]. Since late seventies, a large number of polymers have been added to the list of conducting polymers such as polypyrrole, polythiophene, polyparaphenylene, polyphenylene sulphide, polyaniline, polyphenylene vinylene etc.
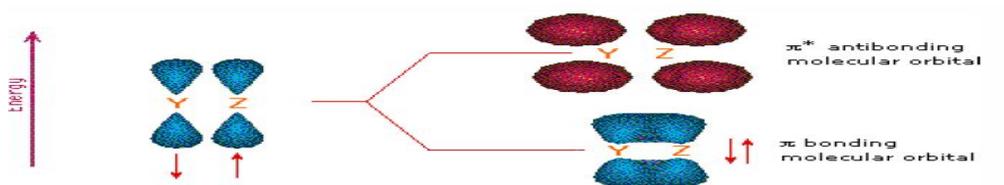

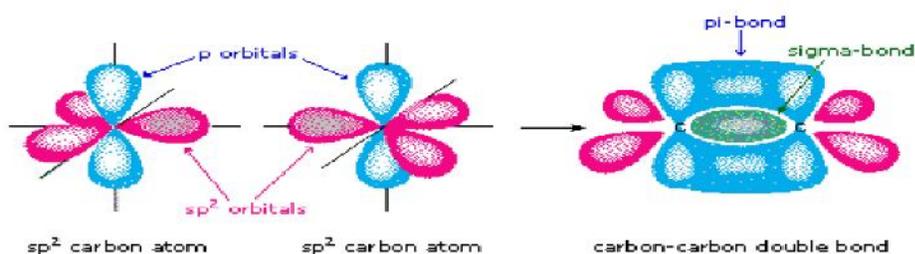*Figure.1.2-A*
π-orbital formation from two p-orbital

Figure.1.2-B
Formation of σ and π molecular orbits from two sp² hybridized carbon atoms

Polyacetylene was the first polymer to be reported. This conjugated organic polymer, could attain high levels of electronic conductivity when oxidized by suitable reagents initiated a significant research [6]. Doping the polymers creates new states (donor or acceptor states), which exist within the band gap, and are energetically accessible to the pi (π) electrons, resulting significant increase in conductivity. In fact, the conductivity of doped polymers may be up to 10 orders of magnitude greater than that of the neutral polymers.

The concept of conductivity and electro-negativity of conjugated polymer was quickly broadened from polyacetylene to include a conjugated hydrocarbon and aromatic heterocyclic polymers, such as poly (p-phenylene), polypyrrole and
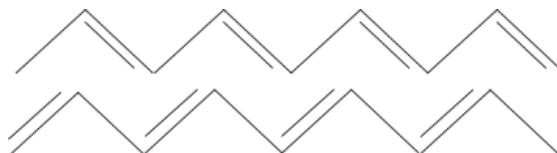

Figure 1.3
Polyacetylene chain

Polythiophene. The conductivity of various doped and undoped polymers, some common semiconductors, and metals is presented in Table 1.1. As the conducting polymers may be doped to various degrees, there is an element of control in doping level, hence the conductivity. This ability to tailor the polymer's electrical properties exemplifies the versatility of conducting polymers.

Table 1.1
Conductivities of Various Con ducting Polymers, Semiconductors, and Metals

Material	Conductivity
Gold,Silver,Copper	$\sim 10^6$
Doped-trans-polyacetylene	$\sim 10^5$
Dopedpolyaniline	$\sim 10^1$
Germanium	$\sim 10^{-2}$
Silicon	$\sim 10^{-6}$
Undoped-trans-polyacetylene	$\sim 10^{-6}$
Undoped polyaniline	$\sim 10^{-10}$
Glass	$\sim 10^{-10}$
Quartz	$\sim 10^{-12}$

1.2 Types of Conducting Polymers

Conducting polymers can be classified in to four different types on the basis of conduction mechanism that renders electrical conductivity to polymers.

- ➢ Conducting polymer composites.
- ➢ Organometallic polymeric conductors.
- ➢ Polymeric charge transfer complexes.
- ➢ Inherently conducting polymers.

1.2.1 Conducting Polymer Composites

Conducting polymer composites are mixture or blends of conductive particles and polymers. Various conductors have been used in different forms together with large number of conducting and engineering plastic. Various conductive fillers have been tried such as carbon blacks, graphite flakes, fibers, metal powders to enhance the electrical conductivity etc. The electrical conductivity of the compound is decided by the volume fraction of the filler. A transition from insulating to non-insulating behaviour is generally observed when volume fraction of conductive filler in the mixture reaches a threshold of about 25%. The various polymers, which have been used as major matrix, are typically Nylon and PVC etc.

1.2.2 Organometallic Polymeric Conductors

This type of conducting materials is obtained by adding organometallic groups to polymer molecules. In this type of materials the d- orbital of metal may overlap

orbitals of the organic structure and thereby increases the electron delocalization. The d-orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it. Metallophthalocyanines and their polymers fall in this class of polymeric material. These polymers have extensively conjugated structures. The bridge transition metal complexes form one of the stable systems exhibiting intrinsic electrical conductivities, without external oxidative doping. These materials possess strong potential for future applications such as molecular wires, antistatic foils and in fibers.

1.2.3 Polymeric Charge Transfer Complexes (CTC)

Polymeric charge transfer complexes (CTC) are formed when acceptor like molecules are added to the insulating polymers. There are many charge transfer complexes reported in the literature, e.g. CTC of tetrathaifulvalene (TTF) with bromine, chlorine etc is a good conductor. The reason for high conductivity in polymeric charge transfer complexes and radical ion salts are still somewhat difficult to understand. It is likely that in polymeric materials, the donor, acceptor interaction promotes orbital overlap, which contributes to alter molecular arrangements and enhanced electron delocalization.

1.2.4 Inherently Conducting Polymers

Research in the field of inherently conducting polymer started nearly three decades ago when 'Shirakawa' and his group found drastic increase in the electrical conductivity of polyacetylene films when exposed to iodine vapour. The highest crystalline variety of the polyacetylene showed electrical conductivity of the order of 10^{-5} S / cm and was in all possibility the trans-form of polyacetylene. Leading on from this breakthrough, many small conjugated molecules were found to polymerize, producing conjugated polymers, which were either insulating or semiconducting in the oxidized or doped state. The electronic properties of conjugated polymers are due to the presence of electrons. The conjugated polymers are studied as the intrinsically conductive polymers (ICP). The conductivity in such polymers arises due to a special type of metallic bonding in which valence electrons are completely delocalized and move almost freely through the crystal lattice. It is therefore necessary for the polymer backbone is necessary for a polymer to behave as an 'electrical conductor'. This delocalization of electrons may occur through the interaction of n-bonded electrons in a highly conjugated chain or by a similar interaction of n-electrons with non- bonded electrons of electron with rich hetero-atoms in the backbone. For this the molecular structure of the backbone should be planar. There should be no torsion at the bonds, which would decrease the delocalization of the electron system. Some of the examples of conjugated polymers are shown in the following Figure1.4.

1.3 Charge Transport in Conducting Polymer

It is well known that polymers with conjugate bonding system, running through the whole molecule are usually electrically conducting. The electrical properties of conducting polymers depend on the electronic band structure. When the bands are filled or empty, no conduction occurs. If the band gap is small compared with thermal excitation energies, electrons are excited to the conduction band and thus conductivity increases. When the band gap is too wide, thermal excitation is insufficient to excite electrons to the conduction band and the material is an insulator. The conductive polymers carry current without having partially empty or partially filled bands. The most important characteristics is that when the polymers are highly oxidized the charge carriers are spinless. To explain the conduction phenomena, it is proposed that when an electron is removed from the top of the valence band by oxidation a vacancy (Hole or radical cation) is created, but it does not delocalize completely. Partial delocalization occurs over several monomer units, and the units deform
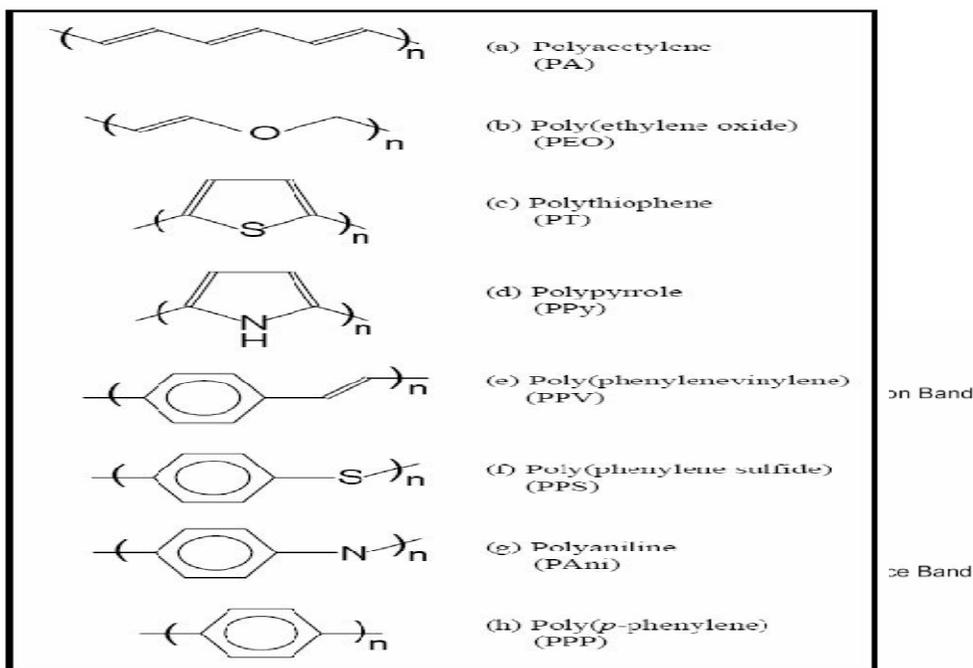

Figure 1.4
Chemical structure of some conjugated polymer some conducting polymers

structurally. The energy level associated with the radical cation represents a destabilized bonding orbital and thus has a higher energy than that of the valence band. A radical cation that is partially delocalized over some polymer segment is called a **'polaron'**. A dication or **'bipolaron'** has two charges associated with the loc oxidation levels yield polarons and higher oxidation levels give the bipolarons. Both polarons and bipolarons are mobile and can move along the polymeric chain by the rearrangement of the double and single bonds in the conjugated system that occurs in an electric field. Conduction by polarons and bipolarons is the dominant mechanism of charge transport in polymers with non- degenerate ground states.

There are several models for electrical conduction in polymers. The most widely used is the one electron band model. This is based on extending the simple model of a bond between two atoms over whole crystalline solid. When two identical atoms each having a half filled orbital are brought together closely enough for their orbitals to overlap, the two orbitals interact to produce two new orbitals, one of lower energy and one of higher energy. The magnitude of this energy difference is determined by the extent of orbital overlap. The two electrons go in to the lower energy orbital. The (now filled) lower energy orbital is a bonding orbital and the high energy (empty) orbital is an antibonding orbital.
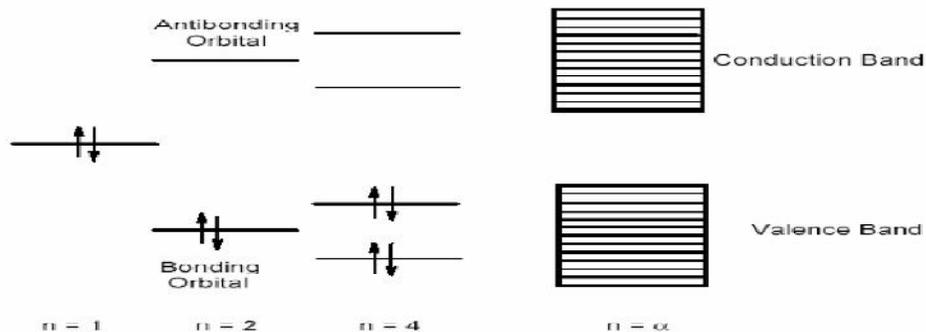

Figure 1.5
One electron band models for electrical conduction

The magnitude of the conductivity is determined by the number of charge carriers at which they move. In order to consider the effect of temperature on the electrical conductivity of the three main classes of materials (metals, semiconductors and insulators), it is therefore necessary to consider its effect on both charge carrier concentration and mobility.

In a 'metal' all the electrons are available for conduction, so the conductivity is determined by the mobility. As the temperature of a crystal lattice is increased, the atoms start to vibrate and interact with the electrons to scatter them. Thus in a metal the electrical conductivity decreases with increasing temperature.

In a 'semiconductor' the same is true, but also the charge carrier concentration increases with increasing temperature. Since the charge carrier concentration is much more temperature dependent than the mobility, this is the dominant factor and hence electrical conductivity increases with increase in temperature.

In an 'insulator' the band gap is so large, so it is very difficult to thermally excite electrons across it to provide charge carriers, and thus at reasonable temperatures the conductivity remains low in insulator.

Conducting polymers are amorphous in nature with short conjugation lengths. Therefore it has been suggested that electrical conduction take place by charge **hopping** between polymeric chains. The electrical conductivity in homogeneous systems can be

well explained by quasiparticle such as polaron, bipolaron and **solitons.** Therefore, transport phenomenon leading to high electrical conductivity. In heterogeneous systems the structure is not uniform but rather a more disordered or branched one. In this type of system the charge transport along the polymer chains take place by hopping.
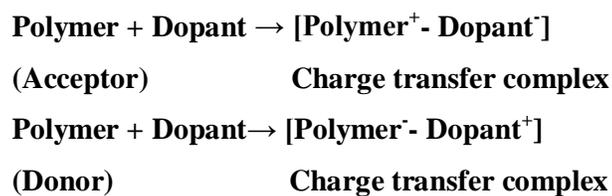
1.4 Doping of Polymers

Conductive polymers generally exhibit poor electrical conductivity ($\leq 10^{-12}$ S/cm) in the virgin state and hence behave as insulators. These virgin polymers need to be treated with a suitable oxidizing or reducing agents to remarkably enhance their conductivities to the metallic region. This phenomenon has been termed as **"doping".** Doping can be simply regarded as the insertion or ejection of charge carriers in polymer. Doping process changes electrical, electronic, magnetic, optical, and structural properties of the polymer.

The doping of conducting polymer involves random dispersion or aggregation of dopants in molar concentrations in the disordered structure of entangled chains. The dopant concentration may be as high as 50%. Also incorporation of the dopant molecules in the quasi one dimensional polymer systems considerably disturbs the chain order leading to reorganization of the polymer. Doping process is reversible, and it produces the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counter ions which stabilize the doped state, may be carried out chemically or electrochemically.

Doping process leads to the formation of conjugation defects, viz. solitons, polarons or bipolaron in the polymer chain. The ultimate conductivity in polymeric semiconductors depends on many factors, viz. nature and concentration of dopants, homogeneity of doping, carrier mobility, crystallinity and morphology of polymers. By controlling the doping level, conductivity anywhere between that of the non-doped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained.

1.5 Dopants

Dopants are either strong oxidizing or reducing agents. On doping, either positive or negative charge carriers are created in polymers.

$$\text{Polymer} + \text{Dopant} \rightarrow [\text{Polymer}^+\text{- Dopant}^-]$$
(Acceptor)   **Charge transfer complex**

$$\text{Polymer} + \text{Dopant} \rightarrow [\text{Polymer}^-\text{- Dopant}^+]$$
(Donor)   **Charge transfer complex**

1.6 Types of Doping

There are various methods which allows for doping of organic materials. The expression doping is ambiguous and refers to an uptake into pure material of some other

material. This uptake may be diffusion of dopants in to the fibers, a chemical reaction with internal or surface chains or simple adsorption on the surface. Doping is accomplished by chemical methods of direct exposure of the conjugated polymer to a charge transfer agent in the gas or solution phase, or by electrochemical oxidation or reduction. The dopant concentration can be determined by chemical or spectroscopic analysis. Doping of polymers may be done by the following methods including [15]

1.6.1 Redox doping

Redox doping is the most common method of doping. This is also known as oxidative doping and accomplished by removing pi (π) electrons from the conjugated pi electrons. All the conducting polymers e.g. PPy, PT, Pani etc. undergo p- and/ or n- redox doping by chemical and/ or electrochemical processes during which the number of electrons associated with the polymer backbone changes. P-doping is accompanied by partial oxidation of the backbone of the polymer. It was first discovered by treating with oxidizing agents such as iodine. p-doping can also be done by electrochemical anodic oxidation by immersing a trans-(CH)x film in a solution of LiClO4 and attaching it to the positive terminal of a DC power source, the negative terminal being attached to an electrode also immersed in the solution. N-doping, i.e. partial reduction of the backbone system of an organic polymer, was also discovered using trans -(CH) x by treating it with a reducing agents such as sodium naphthalide.

1.6.2 Photo Doping

When Trans (CH) x is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap and polymer undergoes "photo-doping".

1.6.3 Charge Injection Doping

Charge injection doping is most conveniently carried out using metal /insulator/ semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. Application of an appropriate potential across the structure can give rise to a surface charge layer. The resulting charges in the polymer, for example, (CH) x or poly (3-hexylthiophene) are present without any associated dopant ion.

1.6.4 Non Redox Doping

Although oxidative doping is available to polyaniline, a more common method of producing doped polyaniline is known as acid- doping (or proton doping). This type of doping differs from redox doping is that the number of electrons associated with the polymer backbone does not change during the doping process. As with the oxidative doping process, doped polyaniline may be produced in one step. The presence of the acid (HA) results in the protonation of nitrogen atoms. Once protonated, the polymer chain is now positively charged, and has associated counter- anions. The degree of

protonation depends on the oxidation state of the polymer and the pH of the acid solution [7]. The energy levels are rearranged during doping. The emeraldine base form of Pani was the first example of the doping of an organic polymer to a highly conductive regime by non-redox type doping. Neutral (or undoped) polyaniline exhibits conductivity on the order of 10-10 S/cm as with oxidative doping, protonic, or acid, doping can result in a significant increase in conductivity (up to 10 S/cm – 11 orders of magnitude) [16]

1.7 Doping Techniques

The polymer made conductive by the doping..Doping in polymers can be done by different ways such as

> ➤ Gaseous doping.
> ➤ Solution doping.
> ➤ Electrochemical doping.

Gaseous, solution and electrochemical doping methods are widely used because of the convenience in carrying out and of low cost. In gaseous doping process, the polymers are exposed to the vapour of the dopant under vacuum. The level of dopant concentrations in polymers may be easily controlled by temperature, vacuum and time of exposure. Solution doping involves the use of a solvent in which all the products of doping are soluble. Polar solvents such as acrylonitrile, tetrahydrofuran, nitro methane are used as solvents. The polymer is treated with dopant solutions. In the electrochemical doping technique simultaneous polymerization and doping generally occurs. But sometimes this method is used for doping for polymers obtained by other methods also. In this process only ionic type dopants are used as the electrolyte in polar solvents.

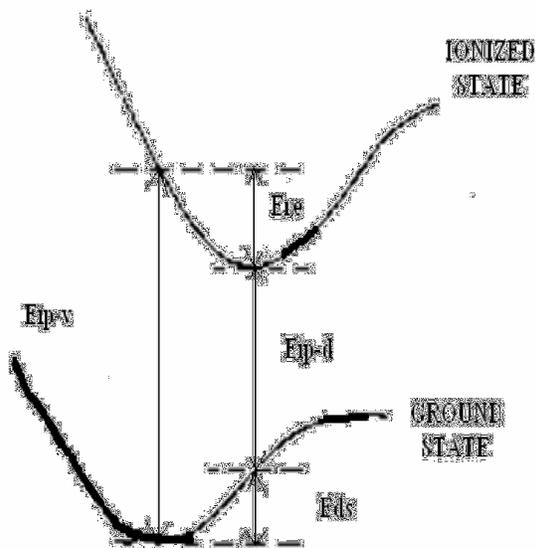## 1.8 Charges on the Polymer Chains

Figure 1.7

Molecular ionization processes in conducting polymer

In a polymer, just as in a crystal, the interaction of a polymer unit cell with all its neighbours leads to the formation of electronic bands. The highest occupied electronic level s constitute the valence band (VB) and the lowest unoccupied levels, the conduction band (CB).the width of the forbidden band , or bandgap (E_g), between the VB and CB determines the intrinsic electrical properties of the material. In organic molecule, it is usually the case that equilibrium geometry in the ionized state is different from the ground state. On ionization of an organic molecule the geometry of the molecule is first distorted in the ground state in such a way that the molecule adopts the equilibrium geometry of the ionized state. This costs distortion energy $E_{dis.}$ Then the reduction in the ionization energy i.e. E_{IP-V} - E_{IP-d} upon distortion is larger than the energy E_{dis} required to make that distortion.

However in an organic polymer chain, it can be energetically favourable to localize the charge that appears on the chain and to have, around the charge, a local distortion (relaxation) of the lattice. This process causes the presence of a localized electronic state in the band gap. Considering the case of oxidation, i.e. the removal of an electron from the chain. This causes the formation of radical ion on the polymer chain and around that charge or cation localization occurs. This radical cation which is formed is having more energy than that of the energy of the valance band. This radical cation associated with the lattice distortion is known as polaron and the presence of localized electronic state in the gap referred to as polaron state. It is having half (1/2) spin [18].
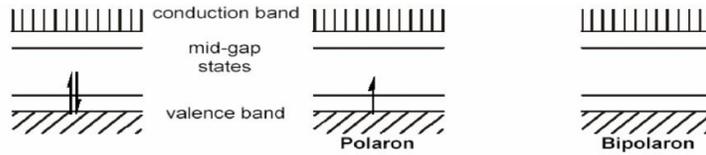
Figure 1.8
Conduction states

A bipolaron is defined as pair of like charges associated with a strong local distortion. It is spineless. The bipolaron charge carrier is of relatively high energy, and thus is short- lived. Redistribution of charge and spin yields a polaron as the more stable charge carrier [18]. A radical, cation, or anion defect on a polyacetylene backbone divides the polymer into sections which are mirror image to each other. The defect can move in either direction without affecting the energy of the backbone. The movement of the defect can be describes as a solitary wave or solitons. The radical defect is referred to as solitons, the anion and cation defects are charged solitons. The neutral solitons is having ½ spin whereas the anion and cation defects are spineless.

1.9 Effect of Doping on Conductivity

The doping process involves transfer of the charge to or from the bonding system of the conjugated polymer, leaving the system essentially intact and hence the structural identity of an individual chain preserved. However, vibrational, electronic and other properties of the polymer are strongly altered upon doping as well as its supramolecular structure. The most spectacular result of the doping is the increase of the polymer conductivity over several orders of magnitude. In some cases conjugated polymers reach the conductivity of metals with a negative temperature coefficient which is characteristic of metallic behaviour. Doping with acceptor or donor molecules causes a partial oxidation (p-doping) or reduction (n-doping) of the polymer molecule. As a result positively or negatively charged quasi-particles are created presumably polarons in the first step of doping. When doping proceeds, reactions among polarons take places , leading to energetically more favourable quasi-particles, i.e. a pair of charged solitons (bipolarons) in a materials with a degenerate ground state. Thus due to the changes in the environment of the chains disorders are created from doping. At low dopant concentration, the dopant molecules occupy random positions between the chains. The effect of the electronic properties by their coulomb potential and by hybridization with the polymers p-orbital. As polarons produced has long lifetime, they are treated as quasi-particles. Polarons have low mobility, which results in obtaining moderate conductivity at low doping concentration. As the doping level is increased, the concentration of polarons goes up and they become crowded together, close enough to form bipolaron. At this point in the doping process, conductivity undergoes a marked increase. Once the radical components of the polarons have combined to form bonds,

the remaining charges achieve high mobility along the chain.

10 Electrical Properties of Conducting Polymers

It is only the doping which makes most of the conjugated polymers conducting from their insulating state to semiconducting or conducting. Although the charged species are incorporated by doping, the electrical conductivity is not ionic but electronic.

Electronic conductivity of conducting polymers depends upon numerous factors. Significant among these are:

➢ Nature or chemical reactivity of the dopant ,

➢ Process of doping,

➢ Doping level,

➢ Method and condition of polymer synthesis

➢ Processing of the polymer

Chemical reactivity of the dopant is of prime importance to obtain a conducting polymer. Not all dopants are equally capable of oxidizing a polymer chain. Iodine is a dopant for increasing the electrical conductivity of polyacetylene by 13 orders of magnitude but is too weak to oxidize PPy or PANI. Similarly HCl is used to conduct PANI. The electrical conductivity of polyaniline hydrochloride observed is 4.4 ± 1.7 S cm^{-1} (59) samples.

Doping conditions also play an important role. Electrical conductivity usually increases with the doping level due to increase in charge carriers concentration. Rapid increase in mobility of the charge carriers may be responsible for this high rate of increase in conductivity. Development of quantitative model for conduction is hampered by the fact that there are at least three elements contributing to the carrier mobility:

- Single chain or intermolecular transport,

- Inter chain transport,

- Interparticle contact,

Electrical conductivity is very much dependent on the method of polymer synthesis, purification of the polymer, physical treatment of the polymer etc.besides nature of the dopants and the process of doping.

1.11 Polyaniline (PANI)

The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields. Among all the conducting polymers, polyaniline is known for its Ease of synthesis, Environmental stability and Easy to dope by protonic acids.

Polyaniline is well- known as an environmentally stable and highly tuneable

conducting polymer, which can be produced as bulk powder, cast films, or fibers. This, in conjunction with the feasibility of low- cost, large- scale production, makes it an ideal candidate for various applications. The term Polyaniline corresponds to a class of polymers having up to 1000 repeat units (also called monomers) and was first reported in 1862 [8]. Much of the structural characterization of polyaniline has taken place in the last 20 years or so, and is fairly well established, although the large number of papers published in the last five years would indicate that polyaniline is still under much scrutiny.

Polyaniline is a typical phenylene based polymer having a chemically flexible – NH- group in a polymer chain flanked either side by a phenylene ring. It can also be defined as the simple 1, 4- coupling product of nonnumeric aniline molecule. The protonation, deprotonation and various other physical -chemical properties of polyaniline is due to the presence of the –NH- group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black. There are several reports of polyaniline found in the literature over the decades about the structure and constitutional aspect of aniline polymerization [9]. In the year 1968, Surville et al [10] reported the proton exchange and redox properties with the influence of water on the conductivity of polyaniline. Polyaniline can be synthesized by both chemical and electrochemical oxidative polymerization.

1.11.1 Structure and Morphology:

There are many levels of polymer structure, and one can categorize the levels loosely using terms used to describe protein structure. The primary structure describes the connectivity of the atoms. The secondary structure describes the three dimensional shape due to short range non-bonded interactions, such as backbone twisting. The tertiary structure describes the shape, also called conformation, of the polymer chains due to long-range non-bonded interactions, which may be inter -chain or intrachain. The term quaternary structure could be used loosely to describe the polymer in terms of degree of order, for example crystalline, semi crystalline, or amorphous.

Morphology is defined as the study of the form. However, when applied to polymers, morphology generally describes the three- dimensional chain conformation and the relationship between chains, as well as the aggregate. Furthermore, morphology includes the physical appearance of polymer the particles such as rice grains, spheres, tubules, and fibrils. Polyaniline exists in four main oxidation states viz. *Leucoemeraldine base, Emeraldine base, Emeraldinesalt, Pernigraniline.*

1.11.2 Derivatives

The presence of non-hydrogen substituents, on the ring or nitrogen atom, has a dramatic effect on the polymer properties. In general, the solubility increases and the

conductivity decrease. In terms of solubility, the increase depends on the nature of the substituents. For example, alkyl and alkoxy substituents result in increased solubility in organic solvents, whereas hydroxyl, carboxylic and sulfonic groups result in increased solubility in water.

It is believed that the decrease in conductivity is a result of two factors: the difference in both size and electronic character of the non- hydrogen substituents. In addition, the electronic nature of the substituents can also affect the conductivity.

1.11.3 Synthesis of Polyaniline

The most common synthesis of polyaniline involves oxidative polymerization, in which the polymerization and doping occurs concurrently, and may be accomplished either electrochemically or chemically. Electrochemical methods tend to have lower yields than chemical yields [11].

A] Electrochemical Synthesis

The electrochemical preparation of conducting polymer dates back to early attempts of Dall'olio and coworkers [12], who obtained "pyrroleblack" as it was called at that time, on electrochemical oxidation of pyrrole in aqueous sulphuric acid as a powdery, insoluble ppt on a platinum electrode. Electrochemical polymerization is regarded as a simple and novel method for synthesis of conducting polymers.

The beauty of this method is that polymerization in suitable electrolytic medium gives directly the directly doped polymer as a flexible freestanding film. In this method, films are produced on the electrode surface by oxidative coupling. In this respect this method is somewhat similar to the electrochemical deposition of metal.
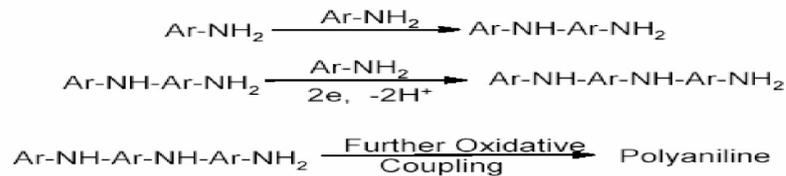
The first electrochemical synthesis of polyemeraldine salt was reported by Letheby [13] in the year 1862. In the year 1962 Mohilner et al [14] reported the mechanistic aspects of aniline oxidation. Major interest in the electrochemistry of polyaniline was generated only after the discovery that aromatic amine, pyrrole, thiophene, furan, and benzene can be polymerized anodically to conducting film. Electrochemically prepared polyaniline is the preferred method to obtain a clean and better ordered polymer thin film.

B] Chemical Synthesis:

Synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulphuric acid in the presence of ammonium peroxo-di-sulfate as the oxidizing agent in the aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate / intermediate or with the final product. However smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. In the many review articles it is reported that the propagation of polymer chains proceeds by a

redox process between the growing chain (as an oxidant) and aniline (as a reducer) with addition of monomer to the chain end. The high concentration of a strong oxidant, $(NH4)_2S_2O_8$, at the initial stage of the polymerization enables the fast oxidation of oligomer and polyaniline, as well as their existence in the oxidized form.

The following figure shows the process of formation of Polyaniline and its various oxidation states respectively.

$$Ar-NH_2 \xrightarrow{\quad Ar-NH_2 \quad} Ar-NH-Ar-NH_2$$

$$Ar-NH-Ar-NH_2 \xrightarrow[2e,\ -2H^+]{\quad Ar-NH_2 \quad} Ar-NH-Ar-NH-Ar-NH_2$$

$$Ar-NH-Ar-NH-Ar-NH_2 \xrightarrow{\text{Further Oxidative Coupling}} Polyaniline$$

Figure 1.6
Formation of polyaniline

2. EXPERIMENTAL PART

The project will initially give emphasis on the study of the conducting polymer and their properties for sensor applications. In second phase, the preparation of conducting polymer films through the chemical synthesis technique will be undertaken, followed by their characterization. The work, then, will be extended towards different organic electronic gas sensing devices.

The scenario of vigorous research in development sensing application has attracted us towards the study on properties of conducting and semiconducting materials for gas sensor. Thus the main aim of this project is to concentrate on the study of conducting and semiconducting polymers for gas / Vapour sensing application.

The conducting polymer polyaniline is prepared successfully by chemical synthesis technique. This process has many parameters such as Concentration of Solution, Concentration of dopants and temperature of polymerization etc. All these parameter affects the conductivity of the conducting polymer polyaniline which will also affect the sensitivity of the film. This process parameter will be varied to obtain the higher conductivity of the conducting polymer Work done so far and results achieved and publications:

In the first phase the conducting polymer polyaniline is prepared with the readily available chemicals in which to oxidize 0.2 M aniline hydrochloride with 0.25 M ammonium peroxidisulphate in aqueous medium. Aniline hydrochloride and Ammonium peroxidisulphate 1:2 ratio was dissolved in 50 mL of double distilled water. Both solutions were kept for 1 hrs.at room temperature, then mixed in a beaker, briefly stirred, and left at various temperatures (00C-150C to polymerize). Next day, the Polyaniline precipitate was collected on a filter paper, washed with three 100 mL

portions of 0.2 M HCl, and similarly with acetone. Then Polyaniline (Emeraldine) powder was dried in air.

Polyaniline prepared under these reaction and processing conditions are further referred to as "standard samples". Additional polymerizations were carried out in an ice bath at 0–2 °C. The acidity of the reaction mixture was increased by replacing 10 ml of water with 10 ml of 10 M HCl in several experiments. The above picture shows the experimental setup in Lab during the synthesis of Polyaniline.

The active layer of sensor is made by depositing the film on the substrate with the help of prepared conducting polymer. The different films will be grown and different dopants will be studied to enhance the sensing properties of different gases. We will concentrate on deposition of films from Poly-aniline conducting polymer. The active layer of conducting polymer acts as a sensing element and reacts with the gas molecule and produce the corresponding change in its conductivity.

Process Flow Chart:
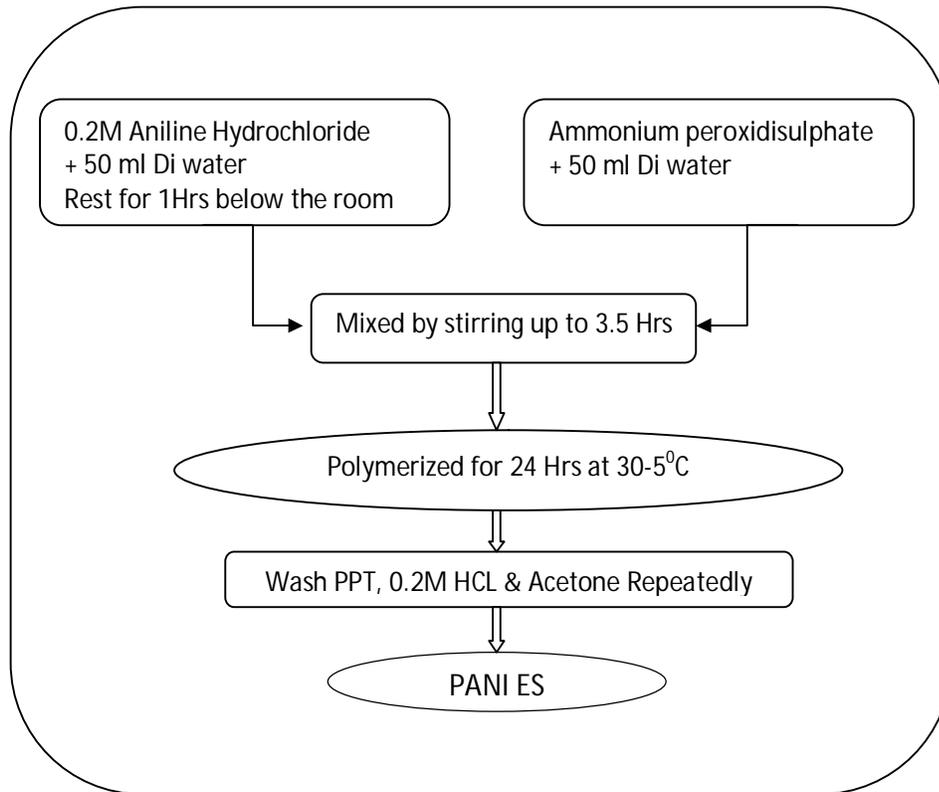
3. Result and Discussion

The synthesis of conducting polymer is done by chemical synthesis technique. After preparation of conducting polymer PANI, a film is formed with the help of spin coating technique. The prepared film is then further characterized for the study of electrical, physical and optical properties. The electrical characterization is done by two probe technique. The optical and Physical property of the synthesized PANI film is studied with the help of UV and FTIR spectroscopy.

After achieving the desired conductivity the prepared film was use for gas sensing application electronics applications. In this work the prepared film was used as an active layer in a sensor for gas sensing application.

Electrical Characterization:
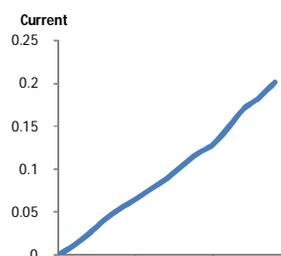
The synthesized PANI films with optimised concentration of monomer, dopant, and oxidant and on different temperatures are subjected to I - V characterization to study the effect of temperature on the ohmic behaviour of the film. The electrical characterization of film is done by the two-probe method at room temperature. The figure.5.10 shows the I-V characteristics PANI films prepared at different polymerization temperatures, which gives the linear relationship between current and voltages. When we increase the applied voltage then the current is increases in proportion with the applied voltage. This reveals that the Polyaniline film has an ohmic behaviour which is good argument with early reported work.

The UV-vis spectrum shown in the following figure is useful for gauging the extent of conjugation - highly conjugated, and therefore conductive, polyaniline samples exhibit a wide absorbance, called a free carrier tail, at wavelengths higher than approximately 700 nm. As the conjugation length increases, the peak shifts to higher wavelengths and becomes very broad. The following figure shows the UV-Visible spectrum of PANI synthesized by chemical synthesis method.
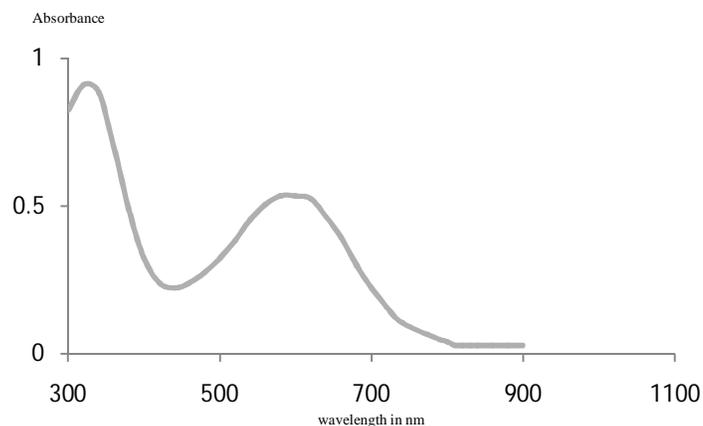
Typically, emeraldine base exhibits absorbance's at approximately 330 nm, due to the Benzenoid π - π^* transition, and at approximately 635 nm, which is attributed to the quinoid exciton absorption .Upon doping, the quinoid transition disappears, and two new absorbance appear. These new absorbance are assigned to polaron and bipolaron transitions. Note that the polaron transition occurs at a higher wavelength (thus lower energy) than the bipolaron transition.

The conducting emeraldine salt has two characteristic absorption bands at 320-328 and 420-440 The peak at 320nm corresponds to the π - π^* transition of the Benzenoid ring, while the sharp trough at 440nm can be assigned to the localized polaron which are characteristics of the protonated Polyaniline, together with extended tail at 700-800nm representing the conducting ES state of Polyaniline All these spectra exhibit strong evidences for the protonation of PAni.
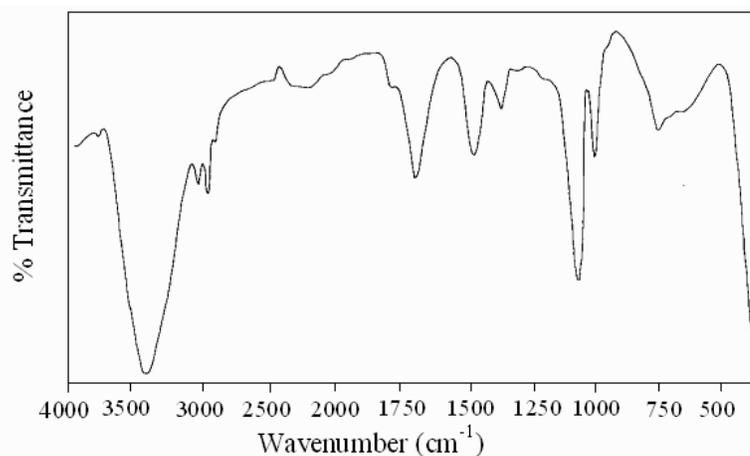
The above Figure shows the FTIR spectroscopy of the synthesized PANI film. The molecular structure of the synthesized PANI film was studied using the FTIR spectroscopy. Formation of the polymers, presence of a functional group on the polymer backbone or change in the protonation -deprotonation equilibrium of Emeraldine can be deduced from the presence of corresponding bands in the FTIR spectrum. It is seen that Quinoid and Benzenoid ring stretching bands are present at 1653 cm−1 and 1423 cm−1. The C-H in plane and C-H out of plane bending vibrations appears at 1024 cm−1 and 952 cm-1. The peak at 1315 cm−1 is assigned to C–N stretching of secondary aromatic amine. In addition, a relative weak peak at 1700 cm−1 appears in the spectrum is due to the stretching vibration of carbonyl group and it shows presence of AA in the film. Band at 3440 cm -1 is assigned to the N-H stretching band. All these characteristic bands confirm the presence of conducting ES phase of the polymer. This shows very good agreement with earlier reported work

• PANI film in gas sensing application

The gas sensing study is carried out under the static gas chamber to sense the ammonia gas. The Polyaniline thin film is used as sensing element. The sensing element is placed on Four-Probe/Two probe assembly in the gas chamber. The known volume and concentration of ammonia gas will be allowed to introduce in the chamber. When chamber is full with gas, the corresponding change in surface resistance of thin film will be recorded.

In this study the efforts were extended to focus on the sensitivity and repeatability of the polymer film. This is achieved by analyzing the change in surface resistance by four- probe and it also depends upon the concentration of exposed ammonia gas in a gas chamber.
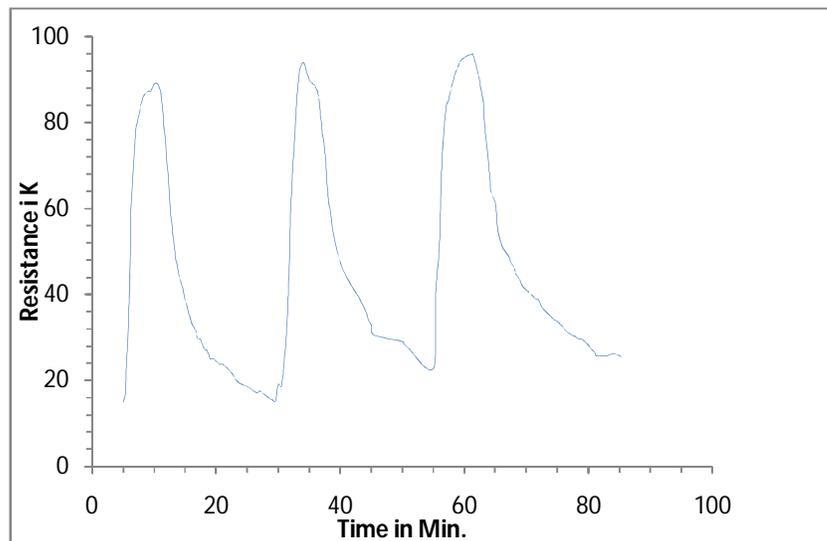
The above figure shows the reputability of the sensor for ammonia gas the reaction mechanism for ammonia is as follows

The protons on –NH- group were transferred to NH3 molecules to form ammonia ions, while Polyaniline itself turned in to its base form. This process is reversible and in a Polyaniline, which has unique feature to react with exposed gas molecules. It shows reversible acid/base doping process. In this process, first emeraldine salt forms and Polyaniline becomes conductive, while the emeraldine base or dedoped polymer becomes insulating materials.
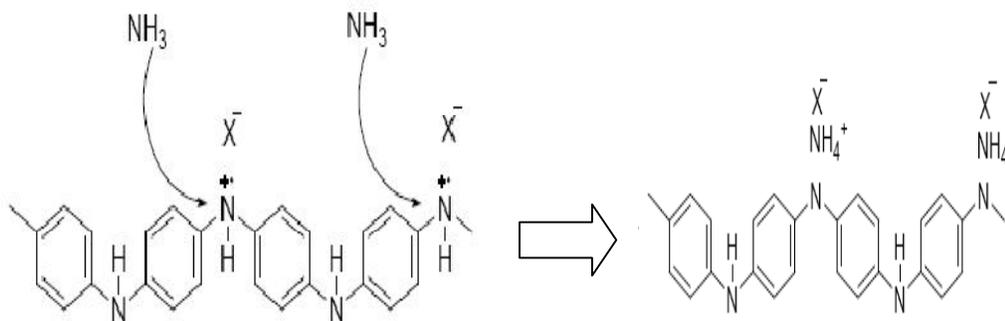
The above figure shows a Doping-dedoping process of PANI with Ammonia gas Polyaniline is a special conducting polymer because its doped state can be controlled by acid / base reactions. This is widely used to detect the acidic/basic gas vapors. When thin film of Polyaniline is exposed to ammonia gas, it undergoes dedoping by deprotonation as shown in the above in fact when ammonia atmosphere is removed, the ammonia ions can be decomposed to ammonia gas and protons.

The sensitivity of the sensor depends upon the reaction time with the gas molecules, which interacts with the film resulting due to the change of surface resistances. The change in resistance of the film depends upon the concentration of

ammonia gas passing per unit time. The surface resistance of the film both pristine and irradiates are plotted as a function of concentration of ammonia gas in specified volume

4. Conclusions:

In the present work Polyaniline has been synthesized by chemical oxidation technique. The electrical, optical and physical properties of PANI films are investigated successfully. According to electrical measurements the conductivity of the polymer is in good agreement at lower temperature with standard values. Further, it can be conclude that the deposited film can be used to prepare efficient active layer for sensors because of its ease in synthesis and environmental stability. Its redox behaviour (doped-dedoped) makes it a potential candidate for chemical sensing element, chemiresistors.

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