CHAPTER 1.....

INTRODUCTION

During the last 20 years, global research and development (R&D) in the field of sensors has expanded exponentially in terms of financial investment, the published literature, and the number of active researchers. It is well known that, the function of a sensor is to provide information on our physical, chemical and biological environment. Legislation has fostered a huge demand for the sensors necessary in environmental monitoring, e.g. monitoring toxic gases and vapours in the workplace or contaminants in natural waters by industrial effluents and runoff from agricultural fields. Thus, a near revolution is apparent in sensor research, giving birth to a large number of sensor devices for medical and environmental technology. A chemical sensor furnishes information about its environment and consists of a physical transducer and a chemically selective layer [1]. Sensor devices have been made from classical semiconductors, solid electrolytes, insulators, metals and catalytic materials. Since the chemical and physical properties of polymers may be tailored by the chemist for particular needs, they gained importance in the construction of sensor devices. Although a majority of polymers are unable to conduct electricity, their insulating properties are utilized in the electronic industry. A survey of the literature [2-5] reveals that polymers have also acquired a major position as materials in various sensor devices among those available. Either an intrinsically conducting polymer is

being used as a coating or encapsulating material on an electrode surface, or a non-conducting polymer is being used for immobilization of specific receptor agents on the sensor device.

1.1 Classification of Sensors :

Sensors are broadly classified into two types. They are –

1. Physical sensors and

2. Chemical sensors.

Among these, chemical sensors are of great importance and have been extensively investigated.

1.2 Importance of Chemical Sensors :

Chemical sensors have the potential to play an influential role in meeting environmental objectives through applications in several sectors. These roles would take advantage of a number of favourable attributes of chemical sensors, such as their relatively low cost, ruggedness, and capability for miniaturization. Examples of applications include augmenting existing monitoring and measurement networks to expand monitoring coverage and to survey areas that may require more detailed monitoring. They could also find application in process control to optimize energy and material use, thereby minimizing emissions, as well as in direct measurement of emissions. To realize this potential, chemical sensors must provide sufficient sensitivity for the required

measurements, results that are free from measurement artifacts and interferences, and adequate long-term reliability, all at a competitive cost. Although, much research has focused on sensors based on SnO_2 technology, other inorganic oxides are receiving increased attention. These include binary oxides, such as oxides of titanium, tungsten, and gallium, and more complex ternary oxides. Compounds having the perovskite structure are among one of the important classes of ternary oxides. A number of studies have focused on the chemistry and physics of the response of these materials to gases as well as vapours. Depending on the conditions, these compounds can behave as n- or p-type semiconductors. Because of their structural similarity, similar mechanisms of interaction with gases are expected to occur for these compounds, although the relative importance of the mechanisms for any specific operating condition would depend, in each instance, on the specific compound. An approach to using these materials as sensors is to operate them at sufficiently high temperatures such that thermodynamically controlled structural changes are induced by ambient gas or vapour concentrations.

1.3 Classical Materials For Sensor Application :

The principle of solid-state sensor devices is based on their electrical response to the chemical environment, i.e. their electrical properties are influenced by the presence of gas phase or liquid phase species. Such a change

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in electrical properties is used to detect the chemical species. Although silicon based chemical sensors, such as field effect transistors (FETs), have been developed, they are not currently produced commercially because of technological and fundamental problems of reproducibility, stability, sensitivity and selectivity.

Table 1.1 provides a list of materials used for the construction of various sensor devices. 'Solid-state sensors' have been made not only from classical semiconductors, solid electrolytes, insulators, metals and catalytic materials, but also from different types of organic membranes. Most solid-state sensors are based on catalytic reactions. This is especially true for sensors based on semiconducting oxides. The oxides themselves can be catalytically active, or catalysts can be added [2] to provide sensitivity, selectivity and rapid response to changes in composition of the ambient gas. Silicon is used in field-effect transistors (FETs), consisting of a thin conductance channel at the surface of the silicon, controlled by the voltage applied to a metal film (a gate) separated from the channel of conductance by a thin insulator layer (e.g. silicon dioxide). The electrical properties of semiconductors are sensitive to the gases with which they are in contact. Taguchi [6] first made a commercial device using the sensitivity of semiconductors to adsorbing gases, with SnO_2 as the semiconductor, to avoid oxidation in air and other reactions. The use of

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Table 1.1 Materials for Various Types of Classical Sensors.

Material	Type of Sensor	Analyte
Semiconductor based solid-state sensors	Si, GaAs	H_2O_2, CO_2, H_2S, propane etc.
Semiconducting metal oxide sensors	SnO_2, ZnO, TiO_2 CoO, NiO	CO, O_2, H_2S, AsH_3, NO_2 N_2H_4, NH_3, CH_4, alcohol.
Solid electrolyte sensors	$Y_2 O_3$ stabilized LaF_3	ZrO_2, O_2, CO_2, SO_2, NO. NO_2 in exhaust gases of automobiles, boilers etc.
Organic semiconductors	Polyphenyl acetylene, phthalocyanine, polypyrrole, polyamide, polyimide	CO, CO_2, CH_4, H_2O_2, NO_x, NO_2, NH_3, chlorinated hydrocarbons

compressed SnO_2 powder rather than a single crystal resulted in a practical device for the detection of reducing gases in air. The semiconductor sensor is based on a reaction between the semiconductor and contact gases, which produces a change in semiconductor conductance. Possible reactions include either the conversion of the semiconductor to another compound, or a change in stoichiometry. Another possible reaction might be the extraction of an electron by oxygen absorbed from the atmosphere, thereby decreasing the conductivity of the semiconductor. Organic vapour, if present in the atmosphere, may produce a regain in the conductivity by reacting with the negatively charged oxygen, becoming oxidized, perhaps to H_2O and CO_2, and the electrons are returned to the semiconductor solid. As a result, the conductivity is higher in the presence of organic vapour than in pure air. This concept provides interesting future guidance towards developing novel sensor materials and devices. Ion exchange between the semiconductor and the gas near the surface might be another possibility for change in the semiconductor property. In solid electrolytes, the conductivity depends on ionic mobility rather than electron mobility, where, the conductivity is dominated by one type of ion only. Therefore, solid electrolytes play an important role in commercial gas and ion sensors. In such sensors solid electrolytes are present as nonporous membranes, which separate two compartments containing chemical species at different

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concentrations on either side. By measuring the potential across such a membrane, one can determine the concentration of the chemical species on one side if the concentration on the other side (i.e. the reference side) is known. Solid electrolytes were used in commercial gas and ion sensors, e.g. yittria (Y_2O_3) stabilized zirconia (ZrO_2), an O_2 conductor at high temperature $(300^{\circ}C)$, for determination of oxygen in exhaust gases of automobiles, boilers or steel melts and LaF_3 for the determination of F_2 even at room temperature. Solid polymer electrolytes (SPEs) are another membranes of interest for detection of ions in solution as the electrolyte in electrochemical gas sensors. With this membrane, water must penetrate the solid before the solid becomes an ionic conductor. Nafion, a perfluorinated hydrophobic ionomer with ionic clusters, has been employed as a SPE for a variety of room temperature electrochemical sensors [7].

1.4 Limitations of Classical Materials :

However, these conventional materials have certain major limitations such as :

1. Work at high temperature conditions.

2. Requires several tedious operations such as mixing, calcinations, sintering, hot pressing etc.

3. Cost is high (preparation requires several steps).

As a result of this, in past few years extra attention has been paid to more challenging area: the development of the synthetic materials that can form the basis for sensors to determine the organic compounds ranging from small amino acids to larger macromolecules such as protein [8]. New organic polymer (conducting polymers) materials have proved extremely useful in this regard. Such organic materials provide a new dimension in sensing, enabling the wider range of species to be determined in more complex environment.

1.5   Advantages of Conducting Polymers :

Conducting polymers can offer a variety of advantages for sensor applications over the metallic or ceramic sensor materials.

- ❑ Conducting polymers are relatively low cost materials.

- ❑ Their fabrication techniques are simple and straightforward.

- ❑ They operate at or near room temperature.

- ❑ Have high sensitivity.

- ❑ Lower detectable limit in the range of few tens of ppm.

- ❑ They have flexibility in molecular architectures such as side chain attachments and modification by charged or neutral particles either in the bulk or on the surface [9-11].

Generally, polymers like polypyrrole, polythiophene, polycetylene, polyaniline and its derivatives have been used as a sensor. Among these materials "Polyaniline" is the most popular material as a sensor due to its many excellent features like processibility, functionality and sensitivity.

1.5.1 Conducting polymers as chemical vapour sensor :

The determination of alcohol is important in industrial and clinical analyses, as well as in biochemical applications. Ukeda et al. [12] presented a new approach in the co-immobilization of alcohol dehydrogenase and nicotine amide adenine dinucleotide (NAD) using acetylated cellulose membrane on glutaraldehyde activated Sepharose and its application to the enzymatic analysis of ethanol. Since conducting polymers gained popularity as competent sensor material for organic vapours, few reports are available describing the use of polyaniline as a sensor for alcohol vapours, such as methanol, ethanol and propanol [13,14]. Polyaniline doped with camphor sulphonic acid (CSA) also showed a good response for alcohol vapours [15-18]. These reports have discussed the sensing mechanism on the basis of the crystallinity of polyaniline. Polyaniline and its substituted derivatives such as poly(o-toluidine), poly(o-anisidine), poly(N-methyl aniline), poly(N-ethyl aniline), poly(2,3 dimethyl aniline), poly(2,5 dimethyl aniline) and poly(diphenyl amine) were found by Athawale and Kulkarni [19, 20] to be

sensitive to various alcohols such as methanol, ethanol, propanol, butanol and heptanol vapours. All the polymers respond to the saturated alcohol vapours by undergoing a change in resistance. The resistance was observed to decrease in presence of small chain alcohols, viz. methanol, ethanol and propanol, an opposite trend in the change of resistance was observed with butanol and heptanol vapours. The change in resistance of the polymers on exposure to different alcohol vapours was attributed to their chemical structure, chain length and dielectric nature. All the polymers showed measurable responses (sensitivity, 60%) for short chain alcohols, at concentrations upto 3000 ppm. Mayes et al. [21] reported a liquid phase alcohol sensor based on a reflection hologram distributed within a poly(hydroxyethyl methacrylate) film as a means to measure alcohol induced thickness changes. Blum et al. [22] prepared an alcohol sensor in which two lipophilic derivatives of Reichardt's phenolbetaine were dissolved in thin layers of plasticized poly(ethylene vinyl acetate) copolymer coated with micro porous white PTFE in order to facilitate reflectance (transflectance) measurements. The sensor layers respond to aqueous ethanol with a color change from green to blue with increasing ethanol content. The highest signal changes are observed at a wavelength of 750 nm, with a linear calibration function up to 20% v/v ethanol and a detection limit of 0.1% v/v.

These layers also exhibit strong sensitivity to acetic acid, which affects effective measurements on beverages.

1.5.2 Conducting polymers as gas vapour sensors :

Conducting polymers have promising applications for sensing gases having acid–base or oxidizing characteristics.

Polyacetylene is doped with iodine on exposure to iodine vapour. Then, charge transfer from polyacetylene chain (donor) to the iodine (acceptor) leads to the formation of charge carriers. Above approximately 2% doping, the carriers are free to move along the polymer chains resulting in metallic behaviour. Later, heterocyclic polymers, which retain the p-system of polyacetylene but include heteroatom bonded to the chain in a five membered ring were developed [23]. Such heterocyclic OCPs include polyfuran, polythiophene [24], and polypyrrole. The intrinsically conducting polymers are p-conjugated macromolecules that show electrical and optical property changes, when they are doped/dedoped by some chemical agent. These physical property changes can be observed at room temperature, when they are exposed to lower concentrations of the chemicals, which make them attractive candidates for gas sensing elements. Nylander et al. [25] investigated the gas sensing properties of polypyrrole by exposing polypyrrole impregnated filter paper to ammonia vapour. The performance

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of the sensor was linear at room temperature with higher concentrations (0.5–5%), responding within a matter of minutes. Persaud and Pelosi [26] reported conducting polymer sensor arrays for gas and odour sensing based on substituted polymers of pyrrole, thiophene, aniline, indole and others in 1984 at the European Chemoreception Congress (ECRO), Lyon, followed by a detailed paper in 1985 [27, 28]. Most of the widely studied conducting polymers in gas sensing applications (Table 1.2) are polythiophene and its derivatives [29, 30], polypyrroles [31, 32], polyaniline and their composites [33-36]. Electrically conducting polyacrylonitrile (PAN)/polypyrrole (PPY) [37], polythiophene/polystyrene, polythiophene/ polycarbonate, polypyrrole/ polystyrene, polypyrrole /polycarbonate [38] composites were prepared by electropolymerization of the conducting polymers into the matrix of the insulating polymers PAN, polystyrene and polycarbonates, respectively. These polymers have characteristics of low power consumption, optimum performance at low to ambient temperature, low poisoning effects, sensor response proportional to analyte concentration and rapid adsorption/ desorption kinetics.

Thus, the literature survey gives an idea that all efforts have been made to fabricate a sensor to sense particular analyte vapours at very low concentrations. However, investigations related to selectivity of the sensor

Table 1.2 Conducting Polymer Sensors and Their Applications.

Polymer used	Field of application
Polyaniline	Estimation of glucose, urea, triglycerides
Polypyrrole	Estimation of glucose
Poly (vinyl chloride)	Estimation of pethidine hydrochloride in injections and tablets
Polyaniline (emeraldine base) Nanocomposite ultra-thin films of polyaniline and isopolymolybdic acid	Humidity, NH_3, NO_2. Can be used to fabricate other molecular devices.
Polyaniline and its derivatives	Sensing aliphatic alcohols.
Polyphenyl acetylene	CO, CO_2.
Phthalocyanine	CH_4, H_2O_2.
Polyamide	NO_x, NO_2.
Polyimide	NH_3, chlorinated hydrocarbons etc.

for specific analyte is less reported. Therefore, in the present work, focus has been laid on the selectivity of the sensor, particularly 'polyaniline', as polyaniline has been widely used as a sensor for various organic vapours such as alcohols, ammonia etc. and for many gases. Therefore, polyaniline has been chosen as a matrix and the transition metal nanoparticles were incorporated inside the Pani matrix so as to obtain metal-Pani nanocomposite and these nanocomposites have been further utilized as sensor for chemical vapours. To understand the concept of nanocomposite, a little background of nanoparticles, methods for synthesizing them and related terminologies would be necessary.

1.6 Introduction to Nanoparticles :

Nanoparticles are constituted of several tens or hundreds of atoms or molecules and can have a variety of sizes and morphologies (amorphous, crystalline, spherical, needles, etc.). Some kinds of nanoparticles are already available commercially in the form of dry powders or liquid dispersions. The latter is obtained by combining nanoparticles with an aqueous or organic liquid to form a suspension or paste. It may be necessary to use chemical additives (surfactants, dispersants) to obtain a uniform and stable dispersion of particles. With further processing steps, nanostructured powders and dispersions can be used to fabricate coatings, components or devices that

may or may not retain the nanostructure of the particulate raw materials. Industrial scale production of some types of nanoparticulate materials like carbon black and polymer dispersion drugs have been established for a long time.

The surface of nanoparticles is of great importance for a number of device applications, since a number of surface defects, such as dangling bonds or deep surface traps and dislocations, determine the details of the electron-hole recombination process, a process which plays a crucial role in optoelectronic device operation. The trapping of electron hole pairs must be either suppressed as in case of photodiodes and solar cells, or enhanced, as in the case of light emitting diodes.

A number of methods to modify the surface of the nanoparticles have been developed, consisting mainly of the so called capping procedure or organic ligand attachment.

1.6.1 Metal oxide nanopowders, compound semiconductors and alloys :

Another commercially important class of nanoparticulate materials are metal oxide nanopowders, such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3) or iron oxide (Fe_3O_4, Fe_2O_3). But also, other nanoparticulate substances like compound semiconductors (e.g. cadmium telluride, CdTe, or

gallium arsenide, GaAs) metals (especially precious metals such as Ag, Au) and alloys are finding increasing product application.

1.6.2 Nanowires and carbon nanotubes (nanorods) :

Linear nanostructures such as nanowires, nanotubes or nanorods can be generated from different material classes e.g. metals, semiconductors or carbon by means of several production techniques. As one of the most promising linear nanostructures, carbon nanotubes can be mentioned, which can occur in a variety of modifications (e.g. single- or multi-walled, filled or surface modified). Carbon nanotubes are expected to find a broad field of application in nanoelectronics (logics, data storage or wiring, as well as cold electron sources for flat panel displays and microwave amplifiers), and also as fillers for nanocomposites for materials with special properties. At present, carbon nanotubes can be produced by CVD methods on a scale of several tons per year and the gram quantities are already available commercially.

1.6.3 Nanolayers :

Nanolayers are one of the most important topics within the range of nanotechnology. Through nanoscale engineering of surfaces and layers, a vast range of functionalities and new physical effects (e.g.

magnetoelectronic or optical) can be achieved. Furthermore, a nanoscale design of surfaces and layers is often necessary to optimise the interfaces between different material classes (e.g. compound semiconductors on silicon wafers), and to obtain the desired special properties. Some application ranges of nanolayers and coatings are summarised in Table 1. 3.

1.6.4 Nanopores :

Materials with defined pore-sizes in the nanometer range are of special interest for a broad range of industrial applications because of their outstanding properties with regard to thermal insulation, controllable material separation and release, and their applicability as templates or fillers for chemistry and catalysis. One example of nanoporous material is aerogel, which is produced by sol-gel chemistry. A broad range of potential applications of these materials include catalysis, thermal insulation, electrode materials, environmental filters and membranes as well as controlled release drug carriers. Generally, there are different approaches for a classification of nanomaterials, some of which are summarised in Table 1.3. The main classes of nanoscale structures are summarized below in Table 1.4.

Table 1.3 Tuneable Properties by Nanoscale Surface Design and Their

Application Potentials.

Surface Properties	Application examples
Mechanical properties (e.g. tribology, hardness, scratch-resistance).	Wear protection of machinery and equipment, mechanical protection of soft materials (polymers, wood, textiles, etc.).
Wetting properties (e.g. Anti-graffiti, anti-fouling, adhesive, hydrophobic, hydrophilic).	Lotus-effect, self-cleaning surface for textiles and ceramics, etc.
Thermal and chemical properties (e.g. heat resistance and insulation, corrosion resistance).	Corrosion protection for machinery and equipment, heat resistance for turbines and engines, thermal insulation equipment and building materials, etc.

Table 1.4 Classification of Nanomaterials With Regard to Different

Parameters.

Classification	Examples
Dimension	
3 dimensions < 100 nm	Particles, quantum dots, hollow spheres, etc.
2 dimensions < 100 nm	Tubes, fibres, wires, platelets, etc.
1 dimension < 100 nm	Films, coatings, multilayer, etc.
Phase composition	
Single-phase solids	Crystalline, amorphous particles and layers, etc.
Multi-phase solids	Matrix composites, coated particles, etc.
Multi-phase systems	Colloids, aerogels, ferrofluids, etc.
Manufacturing process	
Gas phase reaction	Flame synthesis, condensation, CVD, etc.

1.7 Methods For Synthesis of Metal Nanoparticles :

Transition metal nanoparticles are generally prepared by two routes –

a] Top – Down Route b] Bottom – Up Route.

Top – Down route reduces the macroscopic particles to nanoparticle size. This route is usually not suited for preparing uniformly shaped nanoparticles, very small sizes are difficult to realize. On the other hand, Bottom – Up procedures are well suited to generate particles with uniform size, shapes and structures. Bottom – Up method starts with atoms that agglomerate in solution or even in gas phase to form particles of definite shape if appropriate conditions are applied.

The metal nanoparticles have a tendency to agglomerate to bigger particles. The process of aggregation leads to a loss in magnetic, electronic, catalytic, or optical properties. To avoid this aggregation, many molecules or compounds are used called as stabilizers. Murry et al [39, 40] used long chain alkyl phosphine R_3P compounds, alkyl phosphine oxides R_3PO, alkyl amines etc. as stabilizers. Burst et al [41] used long chain alkyl ammonium substituents as stabilizers in two-phase reduction method. Here, capping of metal nanoparticles by reverse micelles is worth mentioning [42]. The inverse micelles method has been employed since 1980 for the preparation of semiconductor and metal nanoparticles. When stabilizing agents attach to

the surface of nanoparticles via covalent, dative or ionic bonds, they are referred to as capping agents. Synthetic organic techniques have allowed the tailoring of head and tail groups of stabilizers or capping agents. Pileni et al [43] have worked extensively in the field of synthesis of metal and semiconductor nanoparticles using reverse micelle method. Recently, synthesis of dendrimer stabilized metal nanoparticles is one of the most flourishing fields in nanoparticle research field as these composites are thought to have applications in various fields [44, 45]. In addition, polymers or co-polymers, for example, polyvinyl pyrrolidinone, polyvinyl alcohol and polystyrene are additional examples of important stabilizers [46-48]. The nanoparticles of transition metals can be synthesized by various methods such as -

1.7.1 Gas phase synthesis :

Gas phase synthesis includes two techniques namely 1) Physical vapour deposition and 2) Chemical vapour deposition. The advantage of the deposition technique is that the nanoparticles are obtained in the purest form and can be readily used for their applications, but they cannot be synthesized in bulk quantity. The technique finds some difficulties in practical applications.

a) Physical vapour deposition :

In this technique, a special instrument called 'Cluster beam generator' is used to prepare metal nanoparticles. It consists of a heating unit where metal targets are evaporated by simple heating or better still by laser irradiation. The flow of atoms then passes through variously constructed slits to focus the beam. Modern techniques utilize mass spectrometric units to separate different particles according to mass, leading to fractions of very uniform particles. Disadvantage of this technique is the lack of protecting skin for particles. Bare metal particles immediately aggregate to polycrystalline powders, owing to thermodynamically preferred metal – metal bonding. Therefore, to overcome aggregation, they should be capped which is achieved in chemical vapour deposition.

b) Chemical vapour deposition :

This technique is similar to physical vapour deposition. In addition, a chemical reaction is carried out between the reagents during the deposition. The advantage being that the metal nanoparticles formed are capped automatically and protected from aggregation. Thus, the generalized procedure involves the reaction of bare metal particles with ligand molecules in the solution [49, 50].

1.7.2 Chemical synthesis :

All chemically based synthetic routes to prepare nanosized metal particles underline a common principle of chemical reduction of positively charged metal ion as a simple ion or as centers of complex in the solution [51, 52]. Solvents used in the solution can vary from highly polar ones like water to highly non-polar such as hydrocarbons or aromatic compounds. The type of reducing agent to be used is decided depending on the nature of metal compound. Commonly used reducing agents are gaseous hydrogen [53], hydridic compounds [54], linear alcohols [55], hydrazine hydrate [56], sodium citrate [57] etc.

1.7.3 Thermal reduction method :

Thermal reduction has proved to be a very successful method for the synthesis of metal nanoparticles. In this method, linear chain alcohols are extensively used to reduce metal ions to metal [58-60]. Other than alcohols, use of N, N – dimethyl formamide as a reducing agent has shown the reduction reaction [61].

$$HCON(Me)_2 + 2\ Ag^+ + H_2O \longrightarrow 2\ Ag^0 + (Me)_2NCOOH + 2\ H^+ \qquad 1.1$$

Also, Choo et. al. [62] have used formaldehyde, ethylene glycol and 2- butoxyethanol as reducing agents in the thermal reduction process of Pd^{2+} to Pd^0.

Reduction of metal ions using sodium citrate in boiling conditions is probably the oldest known method, still in use for the synthesis of metal nanoparticles. Sodium citrate performs two functions, that of a reducing agent as well as a stabilizer for metal nanoparticles by forming an electrical double layer around the particles. Thermal decomposition of organometallic compounds is another method worth mentioning for synthesis of metal nanoparticles [63] for example, thermal decomposition of metal isopropoxides or complexes like Pd $(dba)_2$, $Pd_2(dba)_3$, $Pt_2(dba)_3$ (where dba stands for dibenzylidine acetone) in presence of hydrogen or carbon monoxide under mild conditions give free ligands and zero-valent metals as nanoparticles. This is referred to as a ligand reaction or displacement from organometallics.

1.7.4 Sonochemical reduction :

Gedanken from Israel has synthesized metal (Pd, Au, Ag etc.) nanoparticles by sonochemical method [64]. In this method, the sample is irradiated with ultrasonic waves. The chemical effects of ultrasound arise from the acoustic cavitations, i.e. the formation, growth and implosive

collapse of bubbles in liquid. The implosive collapse of bubbles in liquid generates a localized hot spot through adiabatic compression or shock wave formation within the gas phase of collapsing bubbles. These hot spots with transient temperatures of ca 5000 K at pressures of 1800 atm lead to the breaking of the big clusters of the desired compound into tiny clusters of nanometer size [65].

1.8 What Makes Nanomaterials Special ?

Their extremely small feature size is one of the same scale as the critical size for physical phenomena i.e. the radius of the tip of a crack in a material may be in the range of 1 to 100 nm. The way a crack goes in a larger scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable. Fundamental electronic, magnetic, optical, chemical and biological processes are also different at this level. Where, proteins are 10 to 100 nm in size, and cell walls 1 to 100 nm thick, their behavior on encountering a nanomaterial may be quite different from that seen in relation to larger scale material. Nanocapsules and nanodevices may present new possibilities for drug deliveries, gene therapy, and medical diagnostics.

Surfaces and interfaces are also important in explaining nanometer behavior. In bulk material, only a relatively small percentage of atoms will

be at or near a surface or interface. In nanomaterials, the small feature size ensures that many atoms, perhaps half or more in some cases, will be near interfaces. Surface properties such as energy level, electronic structures and reactivity can be quite different from interior states and gives rise to quite different properties.

Thus, the dimension between 1 to 100 nm is referred to as magic dimension, where quantum chemistry and classical laws of physics become inapplicable. This dimension serves to bridge the gap between molecules and condensed matters. Any kind of size variation in this range gives different physical and chemical properties.

1.9 Introduction to Polymer Based Nanocomposites :

At present, a wide range of polymer based devices such as light emitting diodes, photodiodes, solar cells, gas sensors, field effect transistors exist which have been developed and intensively studied in research groups and R and D centers all over the world, some of them are even produced commercially in pilot scale series [66].

1.9.1 Advantages of polymer based devices :

What are the advantages of the polymer based devices that have attracted so much interest from the electronic manufacturers and researchers? The following lists some of them :

1. Low cost production, usually by synthetic methods rather than by microelectronics based "clean" technology ,

2. Low cost of materials used for the device fabrication ,

3. Possibility of facile and non-expensive manufacture of the large area devices such as LEDs or photovoltaic cells ,

4. Availability of totally new morphologies and device geometries, unattainable by traditional microelectronic technology methods ,

5. Opportunity to make devices based on totally new principles such as bistable memory switches, neural networks, adaptive circuits, cellular automata, etc. ,

6. Possibility to realize nanoscale size for the device structural elements without significant efforts especially using self assembly based techniques ,

7. Enormous possibilities to vary the composition and hence the properties of the organic and polymer materials used as device components.

All the advantages outlined make organic and in particular, polymer based devices very attractive at their present stage of development in microelectronic and photonic technology.

When speaking of nanocomposite based devices, one should mention a significant feature which makes them different to fully organic based ones namely, the improved long term stability. The stability of most polymer nanocomposite devices exceeds that of fully organic based devices dramatically, making them especially attractive for application purposes [67].

Another advantage of polymer nanocomposites is the possibility of obtaining p-n nanojunctions, which are impossible in polymer-polymer systems, in particular, junctions between highly doped semiconductor particles, allowing the "fractalization" of the space charge layer, interpenetrating networks of nanoparticles and other valuable properties for device operation and peculiar material morphologies.

Besides the advantages outlined above, the opportunity to tailor the band gap simply by changing the size of the nanoparticles, representing such physical objects as quantum dots, provides an opportunity for the easy manipulation of LED photodiode characteristics. The light emission wavelength, for example, can be operated over a much broader range than by changing the stoichiometry of the binary or ternary chalcogenides traditionally used as inorganic LED materials.

Due to the fact that the size of the nanoparticles can be made less than half that of the visible light wavelength they do not scatter light by Rayleigh mechanism, thus the composite media can be almost as non-scattering as a single crystal. However, in contrast to single crystals, optical properties such as refractive index can be tailored simply by changing the concentration of nanoparticles in the polymer matrix.

The other distinctive feature of polymer nanocomposites is the extremely high interface area between the nanoparticles and the polymer matrix. This determines many of the specific properties, which can be both useful in sensor applications as well as for device operations.

1.10 Scope of The Present Work :

Polymers have traditionally been considered as good electrical insulators and a variety of their applications have been based upon this insulating properties. However, in recent years considerable attention has been dedicated to the development and characterization of new materials with uncommon properties. Among these new 'strategic materials' conducting polymers namely systems combining a plastic nature with a high electric transport have reached a prominent position in terms of numbers of academic and industrial laboratories. Enormous advances have been made during the past decade in the basic science and potential applications of these polymers and their derivatives. The excellent characteristics accompanied by unique technological applications have made polyaniline a center of attraction. Thus, polyaniline have been used extensively as chemical vapour sensor. However, Pani appears to be sensitive to several vapours and it exhibits a very good sensitivity. Therefore, in present work nanocomposites of polyaniline have been synthesized.

Therefore, the present work is focussed on the synthesis of nanocomposites of conducting polyaniline with Pd, Ag and Au nanoparticles. The synthesized nanocomposites have been utilized for chemical vapour sensing so as to obtain polyaniline sensor which would be

highly selective. Indeed, the results demonstrate that each of the nanocomposite is selective to a single chemical vapour even when exposed to a mixture of vapours.

Further, advancement need to be made to tailor-make the materials to yield the prototype sensor for a single analyte vapour. It is worth believing that these materials would substitute the existing technology with their ability to sense under ambient conditions.