CHAPTER -I

Introduction
1.1. Introduction

Gas sensors play a vital role in environmental protection and safety by detecting, monitoring and controlling the hazardous and poisonous gases which are present at very low concentration in the atmosphere. Also, gas analysis of human expiration provides important information on the state and functioning of different human organs, decompensation of some pathologic states or exacerbation of chronic diseases. For example, a quantitative determination of $O_2$ and $CO_2$ in the expiration characterizes gas-interchange functions of the blood and lungs. One of the important methods in medical diagnosis of diabetes, allowing performance of an adequate therapy is the determination of acetone concentration in the blood of a sick person. This is usually made with the help of paper indicators changing their colour under contact with the urine of the sick man. This method has obvious shortcomings in the application; moreover, the constraint between the concentrations of acetone in urine and in blood is of a more complex character than the correlation of those parameters in expiration and in blood because the blood directly participates in the gas-exchange [1]. Since, ethanol vapour is one of the most popular gases in our daily life and industry, it is important to detect and control ethanol vapour. A more positive application of an ethanol vapour sensor may be a breath alcohol checker to monitor ethanol vapour in human breath, which is correlated with the ethanol concentration in a drunk driver’s blood [2].

Use of conducting polymers for gas sensing applications has been an important topic for quite some time. However there are two significant problems; namely, sensitivity to water vapour and poor sensitivity to hydrocarbons and other hydrophobic molecules. For instance, the humidity responses of conductive polymer sensors are sometimes so high that the small signals produced by important volatile gases are lost, leading to a lack of discrimination [1].
A gas sensor should have the following three important properties;

- Sensitivity
- Selectivity and
- Durability

In order to attain high response and excellent selectivity, different approaches such as microstructure control, additives, physical or chemical filters, operating temperature, etc have been adopted to modify the sensing properties of semiconductor metal oxide gas sensors [3]. An increasing number of gas sensor devices are nowadays found to be based on semiconducting metal oxide thin films as the gas-sensitive material. The choice of metal oxides have several advantageous features such as simplicity in device structure, low cost of fabrication, robust nature in practical applications and adaptability to a wide variety of reductive or oxidative gases [4]. It is well known that the sensing mechanism is based on the surface reaction of the particles with the exposed gas (adsorption and desorption of the test gas). As the adsorption is a surface effect, one of the most important factors to change the sensitivity of the sensor material is the surface area. The response of gas sensors can also be improved by decreasing the particle size of the gas sensing material in order to increase the number of oxygen sites on its surfaces. So the nano-sized materials are desirable to enhance the gas sensing properties of semiconducting oxides [3].

The change in the conductivity can generally be explained by two mechanisms; the transfer of electrons from the adsorbed gas to the oxide semiconductor, or the reaction of the adsorbed gas with previously chemisorbed surface oxygen. The main goal of research on gas sensors is to find thin films with good electrical properties for specific sensing applications such as sensitivity in the ppb range and reliable selectivity of gases. For this purpose, intensive studies and investigations on a variety of materials have been conducted to produce different gas sensors [5].
1.2. Metal oxide semiconductors for gas sensors

Metal oxide semiconductors are the most commonly used sensing materials and are the most promising devices among the solid state chemical sensors. They could be used in environmental monitoring, automotive applications, industry production and control and sensor network [6]. Nearly 145 years ago, it was identified that semiconductors are sensitive to gases; from that time a great amount of research has been carried out in order to realize commercial semiconducting devices for gas detection [7]. A sensor detects a change in the gas atmosphere from a change in the electrical resistance of an element. In general, a chemical sensor consists of two functions; the receptor function, which recognizes a chemical substance at the surfaces of the semiconducting particles and the transducer function, which transduces the chemical signal on the semiconductor surface through the microstructure of the sensing semiconductor material into the electric output signal. The change in resistance or current or voltage across the sensing element is recorded as the signal [1].

Table 1.1 shows the sensing behaviour of the gas species with different metal oxides. The surprising aspect of tin oxides is that this material is sensitive to almost all the gaseous species. This gives rise to cross-talk problem if they are present simultaneously in the environment under study. The interaction of all gas species gives rise to mixed signal and the authenticity of sensor signal, based on these materials is questionable and may lead to erroneous conclusions [1]. Apart from sensitivity and stability selectivity is also an important factor which has been taken into consideration in the present work.

1.2.1. Principle behind semiconductor gas sensor

The basic principle of operation of a semiconductor gas sensor is the control of the surface and/or interface potential barrier by adsorbed radicals (surface-charge or work function change) [8].
Table 1.1. Sensing behaviour of different metal oxides to various gaseous species

<table>
<thead>
<tr>
<th>Gas</th>
<th>Metal oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone (CH₃CO-CH₂)</td>
<td>X</td>
</tr>
<tr>
<td>Acetaldehyde (CH₃CHO)</td>
<td>X</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>X X X X X X X X X X X X X X</td>
</tr>
<tr>
<td>Arsenic (AsH₃)</td>
<td>X</td>
</tr>
<tr>
<td>Automobile exhaust gases</td>
<td>X</td>
</tr>
<tr>
<td>Benzene (C₆H₆)</td>
<td>X</td>
</tr>
<tr>
<td>Butane (C₄H₁₀)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Butanol</td>
<td>X</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>X X X X X X X X X X X</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>X X X X X X X X X X X X X X X X X X</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
<td>X</td>
</tr>
<tr>
<td>Dimethyl disulfide</td>
<td>X</td>
</tr>
<tr>
<td>Dimethyldimine (DMA)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Ethane (C₂H₆)</td>
<td>X</td>
</tr>
<tr>
<td>Ethanol (C₂H₅OH)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Humidity (H₂O)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Hydrocarbons (HC)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Hydrogen sulfide (H₂S)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Hydrophobic Gases</td>
<td>X</td>
</tr>
<tr>
<td>Liq. Petroleum Gas (LPG)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Methanol (CH₃OH)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Methyl mercaptan (CH₃SH)</td>
<td>X</td>
</tr>
<tr>
<td>NO, NO₂, NO₃</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>o-xylene</td>
<td>X</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Petroleum/Gasoline</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Phosphine (PH₃)</td>
<td>X</td>
</tr>
<tr>
<td>Propane (C₃H₈)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Propanol (C₃H₇OH)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Smoke</td>
<td>X</td>
</tr>
<tr>
<td>Sulfur dioxide (SO₂)</td>
<td>X X X X X X</td>
</tr>
<tr>
<td>Trimethylamine (TMA)</td>
<td>X X X X X X</td>
</tr>
</tbody>
</table>
In semiconductors the extent of the space charge layer (which controls the electrical conductivity processes) depends on the Debye length:

\[ L_D = \left( \frac{kT\varepsilon}{q^2n} \right)^{1/2} \]

where, \( k \), \( T \), \( q \), \( \varepsilon \) and \( n \) are the Boltzmann constant, absolute temperature, electron charge, dielectric constant and charge-carrier concentration respectively. For semiconductors, the order of magnitude of \( L_D \) is in the micrometer range and comparable to the characteristic extent of the structure (grain size or layer thickness).

In the case of insulators \( L_D \) is very large because of the very low value of the charge-carrier concentration. Moreover, it is not an easy job to measure the conductivity of the insulators: the measured data depends on many non-reproducible parasitic factors. For this reason insulating materials are not suitable as gas sensitive resistors. In degenerate semiconductors and metals, \( L_D \) is comparable with the atomic dimensions; thus only ultra thin layers can give a sensitive device [9].

It has been found that the sensing properties for metal oxides depend on several factors, such as surface area and surface states, as well as the efficiency with the test gas molecules adsorbed on the surface [10].

1.2.2. Role of thin films and nanoparticles

Increase in surface area to volume ratio with decrease in grain size is also very important in the field sensing. At such small length scales most of the atoms are surface atoms, thus significantly increasing the effective number of sites available for reactions. Reduction in grain size plays a very important role in applications that involve surface reactions like catalysis, chemical gas sensing etc. The other factor that becomes predominant at smaller grain sizes is the depletion layer depth, otherwise called as the Debye length \( (L_D) \). For most nanostructures this value is comparable to the diameter (in the case of spherical particles / nanotubes / nanowires) or their width (in the case of nanobelts and other flat nanostructures) [11]. Gas sensors in the form of thin or thick films seem to be more promising detectors over the pellet
form, because they are potentially of low cost, rugged and have low consumption of electrical power [1]. Gas sensors with a thin sensing layer are interesting for the realization of these detectors on industrial scale. In general, polycrystalline thin films exhibit better performance than single crystals or large grain films. Moreover, oxide thin films exhibit a significant change in their conductivity when a change in the ambient occurs, and this property forms the basis for a new generation of gas detectors down to the ppb range [5]. To achieve a better sensitivity, controlling the morphological properties of materials during synthesis is of great importance, as these structural characteristics strongly influence their performance and purpose [12].

Nanoscaling is another way to improve the properties of these materials or to achieve new properties. The attempt to reduce the particle size for the sensing layer to the nanometer range is the new challenge of the research on gas sensors. In fact, a promising effect on gas response characteristics was attributed consequently to nanosizing [13]. Due to a high specific surface area, semiconductor nanoparticles are very well suited to the fabrication of chemical gas sensors by screen printing technology. In nanosized materials, a large fraction of the atoms is present at the surface, and hence, the surface properties become dominant. Hence for the application of semiconducting metal oxide, as a sensing layer material for gas sensors, nanosized particles are desirable [14]. Indeed, the large density of molecules which can possibly adsorb on the semiconductor nanoparticles, results in large variations of the electrical conductivity. Moreover, the reduction of the particle size may eventually lead to a particle radius comparable to the Debye length. As a result, the electron-depleted region can possibly develop in the whole particle, thus inducing drastic resistance variations. However, at nanometer size, the control of the surface structure and surface chemical composition is a necessary prerequisite for ensuring reliable and reproducible properties of semiconductor nanoparticles and nanostructured devices [15].

As the sensing mechanism of metal oxide gas-sensing materials is based on the reaction between the adsorbed oxygen on the surface of materials and the gas molecules to be detected, the state and the amount of oxygen on the surface of materials are strongly dependent on the microstructure of materials, namely, specific area, particle size as well as the thickness of the sensing film. In order to obtain gas
sensors with good performance, most recent research works were devoted to nanomaterials because nanomaterials have high specific area and contain more grain boundaries [7]. Nanomaterials may be in or far away from thermodynamic equilibrium [16]. The laws of the quantum physics rather than those of classical physics, come into play at these small particle sizes and the behaviour of the surfaces start to dominate the bulk behaviour of the materials [17]. Nanostructured materials usually display chemical and physical properties that differ from those of the bulk materials and are promising for the fabrication of novel nanodevices [18]. Significant interest has been generated during the past decades in the field of preparing nanostructural oxides for various applications [19].

Nanoscaling plays a fundamental role on structural (particle shape factor and plane exposure), electronic and adsorption-desorption parameters, all factors influencing the sensing characteristics [13]. Fig. 1.1 shows the geometries, electronic band pictures and equivalent circuits of sensing layers [20]. In the Fig. 1.1 $E_C$ represents minimum of the conduction band; $E_V$ represents maximum of the valence band and $E_F$ represents Fermi level.

1.3. Transparent conducting oxides

The interest in transparent conducting oxides (TCOs) for technological applications is a result of their high infrared reflectance, high luminous transmittance and good electrical properties. These characteristics make TCOs attractive in many areas such as transparent electrodes for solar cells and flat panel displays and coatings for architectural glasses. Moreover, these materials are also promising for gas sensors due to their low dimension, portability and simplicity. The electrical properties of thin films made from TCO materials are strongly influenced by the presence of oxidizing gases. Gas molecules interact with the surface of the film inducing redox reactions to take place, altering the film’s conductivity [21].
The improvement of gas sensing characteristics through chemical composition control of metal oxide is the main approved approach for the design of advanced sensors. A large number of articles are devoted to study the properties of doped metal oxides. However, till now many important problems remained unresolved [22]. Indium oxide semiconductor sensors have been successfully used for the detection of oxidizing gases such as O\textsubscript{3} and NO\textsubscript{2} in the concentration range between some ppb and ppm.

### 1.4. Indium Oxide

Indium oxide (In\textsubscript{2}O\textsubscript{3}) films have been studied for a long time. This material is widely used for the design of transparent conducting electrodes for solar cells and flat panel displays. However the study of gas sensing properties of this material started only 10-15 years ago. As a result many issues related to understanding the mechanism of this material's sensitivity to gas remain unknown and the topic of lively debate [23]. Two crystal structures have been reported for In\textsubscript{2}O\textsubscript{3}; body centered cubic and
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(meta-stable) hexagonal. Cubic form of $\text{In}_2\text{O}_3$ is stable even at higher temperatures whereas hexagonal form is stable at lower temperatures [1]. The reported results for the sensing property of the hexagonal form of $\text{In}_2\text{O}_3$ are very few compared to that of cubic $\text{In}_2\text{O}_3$. This may be due to the stability of the cubic structure even at higher temperatures rather than the metastable hexagonal structure. $\text{In}_2\text{O}_3$ single crystal has the cubic bixbyte structure (also called c-type rare earth oxide structure) and belongs to the space group ($T_h^7$, Ia3). The lattice parameter of $\text{In}_2\text{O}_3$ is 10.117 Å. The coordination is six fold for the In atoms and four-fold for the O atoms. Fig. 1.2 shows the ideal representation of the basic unit of the $\text{In}_2\text{O}_3$.

![Fig. 1.2 Ideal representation of the basic unit of the $\text{In}_2\text{O}_3$ network.](image)

One can assume that there are two crystallographically non-equivalent In sites. One of these is associated with an In-O separation of 2.18 Å, and O atoms lying nearly at the corners of a cube with two body-diagonal opposite corners unoccupied. The other is associated with non-equal In-O separations of 2.13, 2.19 and 2.23 Å, and O atoms lying nearly at the corners of a cube with two face-diagonal opposite corners unoccupied. The unit cell contains 80 atoms and as such, the structure is highly complicated. Due to this, band structure calculations of $\text{In}_2\text{O}_3$ have not been made. However, Hamberg & Granqvist and Fan & Goodenough have proposed a simple band structure to explain the conduction mechanisms in $\text{In}_2\text{O}_3$ [24]. According to Hamberg and Granqvist, the assumed band structure (Fig. 1.3) has parabolic bands characterized by effective mass $m_e^*$ for the conduction band and $m_v^*$ for the valence band. The direct band-gap denoted by $E_{g0}$ is 3.75 eV. The dispersions for the valence and conduction bands are given as
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$$E_{v}^{o}(k) = \frac{-\hbar^{2}k^{2}}{2m_e}$$

$$E_{c}^{o}(k) = E_{go} + \frac{\hbar^{2}k^{2}}{2m_e}$$

where $k$ is the wave vector. Superscript $o$ denotes unperturbed bands, i.e. for undoped $\text{In}_2\text{O}_3$. On the basis of the controlled valence representation of Vincent, Fan and Goodenough suggested that the conduction band is mainly from In:5s electrons and the valence band is from O:2p electrons. For stoichiometric $\text{In}_2\text{O}_3$ the Fermi energy $E_F$ is located half-way between the energy bands. Usually $\text{In}_2\text{O}_3$ is somewhat reduced, and these oxygen vacancies, symbolized as $V_o$, give rise to shallow donor states just below the conduction band. In oxygen deficient $\text{In}_2\text{O}_3$ samples, $E_F$ lies between the donor levels and the conduction band minimum. $\text{In}_2\text{O}_3$ is a non-stoichiometric compound under various conditions, with an In/O ratio larger than 2/3. This non-stoichiometry results in an n-type semiconductor or even a semimetal at high electron concentration. During crystal growth, a large number of native donors are produced because of oxygen vacancies. These donors also create an intense free-carrier absorption in the infrared reflection spectrum. All the fundamental vibrational modes at the $\Gamma$ point ($k=0$) are decomposed into irreducible representation as

$$\Gamma\text{_{vib}} = 4A_g + 4E_g + 14T_g + 5A_u + 5E_u + 17T_u$$

where the $17T_u$ modes are infrared active and the $4A_g$, $4E_g$ and $14T_g$ modes are Raman active. One of the $17T_u$ modes is acoustic, while the remaining 16 are optical. Twelve infra-active modes were observed in their measurements and the other four modes were too weak to be observed.

Indium oxide has been widely used in the microelectronic field devices such as gas sensors, window heaters, solar cells, memory devices and flat panel display materials. For example, $\text{In}_2\text{O}_3$ nanowires and nanorods have been employed to fabricate field-effect transistors, nanoscale chemical sensors for the detection of NO$_2$, NH$_3$, acetone, DNA, bio-sensing devices, etc. However, the greater possibility of applications of $\text{In}_2\text{O}_3$ nanostructures depends on controlled synthesis of these materials with specific morphologies [25]. Different $\text{In}_2\text{O}_3$ morphologies such as nanowires, nanobelts, nanoparticles, nanotowers, microarrays, nanotubes, nanocables,
lotus-root-like $\text{In}_2\text{O}_3$ nanorods and nanocolumns, nanocrystal chains and hollow spheres have been prepared via well-developed methods such as the chemical vapour deposition.

\textbf{Fig. 1.3} Assumed band structure of undoped $\text{In}_2\text{O}_3$. Shaded area denotes occupied states. Band-gap and dispersion relations are also shown

There is no universal law describing the influence of doping on the gas sensing properties of metal oxide sensors. Each dopant has its own specific nature, depending on the type of introduced impurity and its concentration, and this should be taken into account in analyzing the results [22].

\textbf{1.5. Survey of Literature}

A detailed literature survey has been undertaken to process the present work and a few are given below;

$\text{In}_2\text{O}_3$ thin film based ozone sensor and the sensing mechanism of the material has been initially investigated by Takada [26] in the year 1989. He reported that the gas sensing mechanism of $\text{In}_2\text{O}_3$ was based on the adsorption phenomena of an ozone molecule on the surface of the sensing film, which increases the film resistance. After his invention many researchers worked and reported about the sensing property of the
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material towards different gases. Chung et al [4] spin coated In$_2$O$_3$ thin films on alumina substrates such that it formed a dense stack of uniform crystallites. They have reported that the formed crystallites showed good sensitivity towards CO and H$_2$ at 350°C but the material’s selectivity by this method has to be improved. In$_2$O$_3$ whiskers and bipyramidal nanocrystals synthesized by Kaur et al [27] using carbothermal method is sensitive to 200 ppb levels of H$_2$S gas at room temperature. Adurodija et al [28] studied the electrical properties of pulsed laser deposited In$_2$O$_3$ thin films. They have reported that the electrical resistivity of the film depends upon the oxidation state of indium. The creation of oxygen vacancies contributed the free electrons that lowered the resistivity of the material. Similarly increase in substrate temperature also lowers the resistivity of the material.

Epifani et al [29] prepared In$_2$O$_3$ nanocrystals with size ranges from 4 to 10 nm and drop coated it over alumina substrates. The prepared film was sensitive to ozone for 60 ppb level at room temperature. They have reported that the enhanced sensing property was the combined effect of the nanocrystal size and surface chemistry, characterized by high densities of oxygen vacancies. A new type of In$_2$O$_3$ based sensor has been constructed by Liess [30]; the device has been reported to distinguish between different gases and their concentration, but still more investigations are necessary to understand the dynamic process. Ko et al [31] observed tunable light emissions from thermally evaporated In$_2$O$_3$. They have reported that the emission was due to the carrier recombination between the valence band and the oxygen vacancy induced donor levels formed in the midst of the In$_2$O$_3$ band gap. The different crystallization qualities of the In$_2$O$_3$ nanostructures could result in different transition path of carriers due to different amounts of oxygen vacancies and defects generated during the growth. Wang et al [32] synthesized In$_2$O$_3$ semiconducting nanowires by chemical vapor deposition method (CVD). The prepared nanowires showed strong red (670 nm) emission at low temperature which was due to the presence of the small amount of oxygen vacancies present in the nanowire crystal structure.

In$_2$O$_3$ thin films were prepared by Winter et al [33] using molecular beam evaporation method and they have studied the gas sensing behaviour of the films at low temperature. The film showed high sensitivity to NO$_2$, CO and CO$_2$. Atashbar et
al [34] prepared In$_2$O$_3$ thin films by RF sputtering and sol-gel method. The sol-gel prepared film showed more sensitivity to ozone molecules than RF sputtered films; this is due to the presence of porous structures on the surface of the films prepared through sol-gel method. The porous structure offered larger surface area and also the film was found to possess oxygen vacancies which were responsible for the high sensitivity of the films.

Wang et al [35] reported the phase selective growth of In$_2$O$_3$ thin films. The optical band gap of the rhombohedral polytype was found to be ~0.7 eV lower than the band gap of the cubic polytype of In$_2$O$_3$. Porous In$_2$O$_3$ thin films were prepared by Ghimbeu et al [36] using electrostatic spray deposition technique (i.e. wet chemical method). Platinum-coated alumina substrates were used for deposition of thin films prepared from indium chloride precursor. Ezhil Raj et al [37] prepared In$_2$O$_3$ thin films through chemical spray pyrolysis method using indium acetylacetonate precursor. The prepared films were preferentially oriented along (222) direction with a nearly constant carrier density of about $10^{20}$ cm$^{-3}$. The films can either be used as conducting or transparent electrodes in optoelectronic devices. Prathap et al [38] deposited In$_2$O$_3$ thin films by chemical spray pyrolysis technique at different substrate temperatures. The layers deposited at 400°C showed a strong (222) orientation and exhibited cubic structure and the layers grown at lower temperature were randomly oriented and less crystalline. Presence of strain in the film could restrict the growth of the grains and influence the optoelectronic properties of sprayed In$_2$O$_3$ thin films.

Optical absorption of In$_2$O$_3$ thin films has been investigated by Novkovski and Tanusevski [39]. They have identified that one direct forbidden (3.29 eV) and three indirect allowed transitions (2.09 eV, 3.42 eV and 3.58 eV) had contributed to the absorption coefficient. They were attributed to the transitions from the valence band to the lowest minima in the conduction band separated from the valence bands by gaps ~2 eV and 3.3 eV largely in agreement with the results of ab initio calculations. High conductivity of In$_2$O$_3$ is due to the generation of carriers by transitions from the valence band to the two lowest maxima of the conduction band, going along with a high transmission in the visible range upto photon energies of ~4 eV, at which direct transitions occur, leading to a strong absorption.
Ho and Yen [40] coated In$_2$O$_3$ thin films using indium sulphate aqueous solution by cathodic synthesis. The transformation of the aqueous solution to In$_2$O$_3$ was studied using TG/DTA analysis. At 300°C indium hydroxide gets transformed to indium oxyhydroxide and at 500°C the oxyhydroxide gets transformed to In$_2$O$_3$. Shigeno et al [41] investigated the formation mechanism and the temperature of In$_2$O$_3$ was examined through TG-DTA-MS analysis. The dip coating solution for the film preparation has been made from indium 2-ethylhexanoate monohydride solution which was taken in aluminium pans for the investigation. They have found that at 500°C the materials gets transformed into In$_2$O$_3$. Korotcenkov et al [42] prepared In$_2$O$_3$ thin films by spray pyrolysis. They annealed the prepared films in an atmosphere of usual air and observed four standard stages: the stage of structural stability of the film (25-500°C); the stage of coalescence of grains forming agglomerates (500-700°C); the stage of local structural reconstruction (700-1000°C) and the stage of global (comprehensive) structural reconstruction (>1000°C). The greater the thickness and the annealing temperature were, the larger was the change of grain size.

The surface structures In$_2$O$_3$ thin films have been studied by Zhou et al [43]. They found that metal-terminated In$_2$O$_3$ surfaces are saturated by chemisorbed O$_2$ dimers, at which point the surfaces become virtually identical to the O-terminated surfaces and the dissociative chemisorption of H$_2$O becomes the energetically preferred process. Single crystalline In$_2$O$_3$ nanowires were synthesized by Wu et al [44] by carbothermal reduction reaction in nitrogen atmosphere. The nanowires emitted blue light (416 and 435 nm) under the excitation at 260 nm and the emission is due to the presence of oxygen and indium-oxygen vacancy centers.

Taurino et al [45] prepared nanostructured In$_2$O$_3$ thin films by wet chemical method (sol-gel). They have shown the compatibility of the wet chemical method with silicon technology. Metal oxide thin films showed good adhesion properties with Si/SiO$_2$ substrate which were dependent on deposition parameters like annealing temperature, starting precursor etc. Cantalini et al [46] prepared In$_2$O$_3$ thin films by sol gel and thermal evaporation methods and detected the sensing behaviour of the thin films towards NO$_2$ gas with the cross examination of ethanol and moisture. They found out that the sensitivity of the film prepared through sol-gel method showed
better sensing property when compared with thermally evaporated films. In$_2$O$_3$ thin films have been prepared by Gurlo et al [47] using electron beam evaporation technique and sol gel method. They have concluded that the sol gel method adapted by them tuned the particle size much lower as well as showed improved sensitivity towards NO$_2$ gas when compared with the electron beam evaporation method.

Tahar et al [48] reported that In$_2$O$_3$ grains have a strong dependence not only on the heat treatment conditions but also on the starting material. They have also reported that the electrical resistivity of In$_2$O$_3$ films obtained from organic solution was lower than that of aqueous sol because of the difference in film density. Lorenz et al [49] synthesized In$_2$O$_3$ nanoparticles at low substrate temperatures. They have prepared the particles without any catalytic activity and at low temperature; oriented pyramidal and octahedral structures were obtained. Korotcenkov et al [50] reported that grain size and porosity are the parameters of In$_2$O$_3$ thin films that best control gas response to ozone. In the detection of reducing gases the influence of film structure is less important. Decrease in film thickness, grain size and degree of texture are the best ways to decrease time constants of the gas response of In$_2$O$_3$-based gas sensors. Xu et al [51] synthesized In$_2$O$_3$ nanowires and nanorods using hydrothermal treatment. Typical diameter of the belt-like nanowires was 30-50 nm and nanorods exhibited an average diameter of about 20 nm. The sensing property for the prepared nano-wires and -rods were tested with NO$_2$ gas and it was found that the nanowires showed 1.5 times larger response than the nanorods. The nanowires samples contained some nanocubes which are helpful to generate grain-boundaries. In contrast, the In$_2$O$_3$ nanorods samples were composed of some uniform nanorod bundles, which are typical large secondary grains with a fewer amount of grain-boundaries and lower response to NO$_2$.

A Longer period of good stability In$_2$O$_3$ nanowire sensor has been attained by Vomiero et al [52]. They have synthesized In$_2$O$_3$ nanowires by vapor-solid mechanism and tested its sensitivity towards acetone in the temperature range between 100 and 500 °C. Chung et al [53] spin coated thin films of indium oxide on silicon and alumina substrates. The gas sensing properties of the films to CO, H$_2$ and C$_2$H$_8$ depended rather strongly on the kind of substrate, film thickness and operating temperature. The best sensing performances to CO was attained with a 160 nm-thick
film (5 times coated) and a 140 nm-thick film (3 times coated) annealed at 350°C on alumina and silicon substrates, respectively. The sensing performances to H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} showed somewhat different dependence on the film thickness. They suggested that the sensitivity and selectivity of the In\textsubscript{2}O\textsubscript{3} film was deeply related with its microstructure.

Epifani et al. [54] used a different approach for the preparation of In\textsubscript{2}O\textsubscript{3} nanocrystals. The prepared nanocrystals were drop coated as thick conductive layers to carry out ozone sensing tests. The sensor showed good response to the gas at ppb levels. Gurlo et al. [55] synthesized thick and thin films using aged colloidal solution and aged precipitate prepared from indium nitrate precursor. Sensors constructed with these films showed good response to ppb levels of ozone molecules and NO\textsubscript{2} gas. Tamaki et al. [56] synthesized micro gas sensor by suspension dropping method over a microgap electrode fabricated by means of MEMS technique and the prepared In\textsubscript{2}O\textsubscript{3} microsensor was sensitive to dilute chlorine gas.

Vygranenko et al. [57] constructed thin film transistor (TFT) with In\textsubscript{2}O\textsubscript{3} over silicon dioxide gate dielectric. When subjected to long-term gate bias stress, the TFT showed faster recovery of the threshold voltage (V\textsubscript{T}) when relaxed without annealing. Thus they suggest that the TFT can be applied for display devices. Zheng et al. [10] fabricated In\textsubscript{2}O\textsubscript{3} nanowire transistor using individual nanowire prepared by chemical vapour deposition (CVD). Room temperature sensitivity of H\textsubscript{2}S at lower concentrations was investigated with a single nanowire transistor. Kim et al. [58] constructed a TFT by spin coating the In\textsubscript{2}O\textsubscript{3} precursor solution on insulated Si substrate and studied its performance. Li et al. [59] constructed a field effect transistor with In\textsubscript{2}O\textsubscript{3} nanowire and reported that the nanowires could be used as active sensing materials and also building blocks for nanoelectronics.

Francioso et al. [60] analysed an micropatterning process of sol-gel SnO\textsubscript{2}, In\textsubscript{2}O\textsubscript{3} and WO\textsubscript{3} thin film for gas sensing applications. They focused on reliable processes for preparation and patterning, which can be further implemented for gas sensor applications. Lavareda et al. [61] synthesized In\textsubscript{2}O\textsubscript{3} thin films by radio frequency plasma enhanced reactive thermal evaporation and constructed it as a transistor and studied its characteristics. Korotcenkov et al. [62] discussed the catalytic
activity of water in In$_2$O$_3$-based thin film gas sensor. Comini et al [63] found that the sensing property of a material can be improved by subjecting the sensing element to UV light. Chung et al [64] synthesized In$_2$O$_3$ porous thin films by sol-gel method and applied it as ozone sensor and have found that the sensor works with stability in air for 6 months. Jeong et al [65] synthesized high quality In$_2$O$_3$ nanobelts without the assistance of any catalyst by physical vapour deposition. The nanobelts emitted visible light around 570 nm with a shoulder at 630 nm when excited with 325 nm. The emission is related to the presence of oxygen vacancies.

The response of In$_2$O$_3$-based thin film gas sensors to CO and NO$_2$ changes with operating temperature and doping and this has been reported by Ivanovskya et al [66]. Wan et al [67] synthesized ITO whiskers and constructed it as a transistor. They found that the nano whiskers are very sensitive to the ambient atmosphere. Ota et al [68] deposited ITO transparent films by dip coating process using indium (III) chloride and tin (II) chloride dissolved in ethanol containing a non-ionic type surfactant (Sorbon T-80). The film thickness was increased by repeating the coating and heating effectively lowered the resistivity of the oxide film to $\approx 2\times10^{-3}$ $\Omega$cm. Post-deposition annealed films in N$_2$--0.1% H$_2$ atmosphere drastically lowered the resistivity to approximately $2.5\times10^{-4}$ $\Omega$cm.

Agashe and Mahamuni [69] deposited heavily doped In$_2$O$_3$: Sn films by the spray pyrolysis technique. They observed that the doping significantly affected the physical properties of the film. As the Sn incorporation was increased, the preferred growth of undoped In$_2$O$_3$ films along $[400]$ was enhanced, up to a doping level of - 36 at. % in solution. For higher doping levels, the films preferentially developed along [222]. This change in preferred growth was proposed to be due to substitution followed by interstitial incorporation of Sn into the In$_2$O$_3$ lattice. Dopant incorporation well as the non-stoichiometry increased linearly with doping. From the electronic transport properties, they have revealed that structural and compositional changes were induced by doping.

The influence upon additions of up to 10 mole% Sn to In$_2$O$_3$ was studied by Agnihotri et al [70]. They have reported that the addition of Sn decreased the resistivity and increases the carrier concentration. Further Sn addition caused the
resistivity to increase and carrier concentration to decrease. The tin additions decreased the lattice parameter which is the indication of the replacement of In\(^{3+}\) ions by Sn\(^{4+}\) ions. The films with low resistivities had a very low activation energy \( (Z \approx 10^{-3} \text{ eV})\) for electrical conduction. The increase of resistivity at higher tin additions is due to poor crystallinity. Manivannan and Subrahmanyam [71] prepared highly conducting \((p = 2.5 \times 10^{-4} \Omega \text{cm})\) and transparent \((92\%)\) ITO films by reactive electron beam evaporation technique. The grain boundary scattering was found to be negligibly small in these films and the average grain size was observed to increase with substrate temperature. The optical band gaps were observed to increase with carrier density. A carrier density of \(7.53 \times 10^{20} \text{ cm}^{-1}\) gave rise to a \(4.01\) eV optical band gap; the evaluated effective electron mass was \(0.67m\) (where \(m\) is the mass of the electron). Daoudi et al [72] synthesized tin doped indium oxide by sol-gel dip coating method and crystallized it using rapid thermal annealing. These films exhibited higher conductivity than those obtained by classical thermal annealing.

Guillen and Herrero [73] sputter coated ITO thin films at room temperature on glass and polyethylene terephthalate which showed polycrystalline structure, with crystallite size and lattice distortion depending on the film thickness and the specific substrate. For the different ITO layers, a general relationship between the electrical characteristics and the structural distortion was found. When the lattice distortion diminishes, the carrier concentration was increased and the electrical resistivity was decreased. On both substrates, enhancement in the crystalline structure and carrier concentration of the ITO coating has been achieved by increasing the film thickness from 0.2 to 0.7 \(\mu\)m. Optical transmittance in the infrared region decreases as the carrier concentration increases, but the average visible transmittance remains about 90\% for a wide range of ITO film thicknesses. Korotcenkov et al [74] studied the influence of additives on gas sensing and structural properties of \(\text{In}_2\text{O}_3\)-based ceramics. The first type of additives \((\text{Cu}, \text{P} \text{ and Mn})\) showed response maxima at lower concentrations of the additives. For the second type \((\text{Ga})\), they observed a linear growth of response and for the third type of additives \((\text{Se} \text{ and B})\) there was no shift of the gas response maxima. Second phase appearance in Raman scattering upon doping was the main factor controlling the change in gas sensing characteristics.
The response improvement of In$_2$O$_3$ thin film towards CO gas has been reported by Lee et al [75]. Yamaura et al [76] have also discussed the improvement in sensitivity of In$_2$O$_3$ thin films towards CO by the addition of 0.5 wt% of cobalt oxide and 0.04 wt% of Au to the sensing film. Gurlo et al [77] synthesized In$_2$O$_3$ and MoO$_3$-In$_2$O$_3$ thin film semiconductor sensors and studied their sensing property towards NO$_2$ and O$_3$. They have reported that the sensor showed good response to the gases at ppb levels. Kuo et al [78] synthesized In$_2$O$_3$ nanorods which were induced by the substrate structure. Commercial anodic aluminium membranes were used as substrates and the nanorods were formed through thermal oxidation of indium chloride solution. Two emissions were observed around 405 and 462 nm; the emission at 405 nm was due to the near band edge emission and the second line was due to the presence of common oxygen vacancies. Zheng et al [79] synthesized In$_2$O$_3$ nanowire arrays as substrates induced structure of anodic alumina membrane. Nanowires emitted broad blue emission which was concluded as an oxygen related defect emission.

Yang et al [80] synthesized indium hydroxide (In(OH)$_3$) and In$_2$O$_3$ nano and micro-particles through micro-emulsion mediated hydrothermal method. They have reported the formation mechanism of the nano-microstructures as an aggregation mechanism. In$_2$O$_3$ nanorod bundles and spheres prepared by them showed similar blue emission peaks around 416 and 439 nm with 383 nm UV excitation. It was mainly attributed to the oxygen vacancies in the particles. Cheng et al [81] reviewed the growth of In$_2$O$_3$ nanostructures prepared from vapor-solid, vapor-liquid-solid method with hot wall CVD. The method is highly controllable allowing the user to easily access different growth regimes. Chu et al [82] synthesized cubic and hexagonal nanocrystals by a simple solution method. The metastable hexagonal structure was prepared through precipitation method. The photoluminescence properties of the products are strongly dependent on their phases, crystallinity and morphologies. Zhuang et al [83] prepared indium oxyhydroxide, In(OH)$_3$ and In$_2$O$_3$, by a liquid phase reaction. They have synthesized different crystal structures such as nanocubes, nanorods, multipods, etc by optimizing the reaction conditions and they have found that the sensor prepared using multipod structure showed good response to ethanol.

Surfactant assisted templating sol-gel process was adapted by Sreethawong et al [84] to synthesize nanocrystalline mesoporous In$_2$O$_3$. Due to the intra and inter-
aggregations of the In$_2$O$_3$ nanoparticles, mesoporous structure has been formed. Chen et al [85] prepared nearly monodispersed particles of tunable sizes (<10 nm) using solvothermal method. The prepared particles emitted UV light (280 nm), which was due the existence of the weak quantum confinement present in the film and while exciting it with 234 nm at room temperature it emitted three strong lines around 469, 544 and 618 nm. Although it possesses weak quantum confinement the emission in the visible range was due to the presence of oxygen vacancies. Tang et al [86] synthesized single crystal In$_2$O$_3$ nanocubes by hydrothermal treatment. Room temperature blue-green emission of the synthesized particles showed the presence of oxygen vacancies in the prepared particles. Zhu et al [87] hydrothermally synthesized In(OH)$_3$ nanorods and microcubes without the addition of any surfactant. The growth mechanism which leads to the shape of nanorods and microcubes were discussed. The reaction was carried out at 200 °C for 20 hr.

Kapse et al [3] prepared pure and Co doped In$_2$O$_3$ nanocrystalline particles and their sensing properties towards H$_2$S gas. They have obtained reproducible sensor with the nanoparticles and the response and recovery of the constructed sensor was a few seconds. Kim et al [88] constructed a nano-floating gate capacitor with In$_2$O$_3$ nanoparticles by embedding the particles in polyimide layer. They have observed memory charging effect at room temperature. Polymer embedded particles have potential application in nano-floating gate flash memory devices. Peng et al [89] synthesized In$_2$O$_3$ nanowires by vapor-solid method at 1030°C in Ar and O$_2$ atmosphere. Green-blue emission at 470 nm was observed due to the presence of the singly ionized oxygen vacancy. Mazzera et al [90] investigated temperature dependent photoluminescent property of In$_2$O$_3$ nanowires. They have reported that the orange emission (630 nm) from the nanowires is due to the presence of intrinsic defects. Maqueda et al [91] synthesized different In(OH)$_3$ nanostructures by precipitation method without the addition of surfactants. The shape can be obtained by maintaining the reaction temperature and aging time, fibre-like structures were formed due to the presence of glycolates.

Zhao et al [92] prepared cubic In$_2$O$_3$ single crystals using solution dispersion method from bulk indium. The prepared nanocrystals emitted ultraviolet blue emission. Baraton et al [93] found that In$_2$O$_3$ nanoparticles with sizes comparable with
SnO₂ possess comparable sensitivity towards CO. In₂O₃ showed more sensitivity to O₂ when compared with SnO₂. Zhu et al [94] synthesized nanoporous In₂O₃ nanocrystal clusters with high surface areas by a one-step solvent-thermal method at a relatively low temperature. They found a deep level emission arising from oxygen vacancies in the PL spectra. Maensiri et al [95] prepared indium oxide nanoparticles by using Aloe vera plant extract as medium. They found a strong emission at UV region and this was attributed to the presence of oxygen vacancies.

UV near band edge emission has been reported by Cao et al [96] for In₂O₃ nanowires prepared using alumina template. The emission peak was observed at 398 nm and they have suggested that the nanowires prepared by this method can be used in optoelectronic devices. Dai et al [97] synthesized In₂O₃ nanowires by a simple gas reaction route in argon atmosphere. They found a strong and wide ultraviolet (UV) emission band centered at around 392 nm and observed photoluminescence at room-temperature in addition to the usual blue emission (468 nm). Xu et al [98] adopted hydrothermal synthesis for the preparation of In₂O₃ nanocubes and identified that the prepared cubes were sensitive to H₂S gas. Du et al [99] adopted surfactant assisted solvothermal method for the synthesis of different nanostructures of In₂O₃. They have also observed blue region emission due to oxygen vacancies.

Zhou et al [100] prepared In₂O₃ nanoparticles dispersed in mesoporous silica and investigated its luminescence properties. They found a broad peak consisting of three peaks at about 430, 480 and 520 nm. Upon calcinating the prepared sample the band reaches maximum value. When the temperature is more than 650°C the whole band red shifts and they have concluded the shift is because of the increase in size of the prepared particles upon calcinating. Fan et al [101] synthesized corundum type In₂O₃ nanostructures through cationic surfactant assisted solvothermal synthesis. They found that the prepared particles showed good response to chlorophenol at 280°C. Hatamie et al [102] synthesized polyvinyl alcohol embedded stannic oxide nanoparticles and applied it for humidity sensors at room temperature. They found that the response and recovery of the sensor is good. Immediately after being taken out of the humid chamber, it regains its original resistance.
1.6. Objective of the present work

The aim of the present work is to prepare a gas sensor with indium oxide thin films and nanostructures. The investigation has been organized as two sections; Section A deals with the preparation, characterization and application of undoped and Sn and Cu-doped In$_2$O$_3$ thin films and section B deals with the synthesis, characterization and application of In$_2$O$_3$ nanoparticles.

1.6.1. The objectives of section A are:

- To synthesize larger surface area of In$_2$O$_3$ thin films on glass substrates by dip coating technique with different precursors and to optimize the method adopted for the growth of tin and copper doped indium oxide thin films.
- To analyze the structure, optical properties, surface morphology, composition and I-V characteristics of the prepared films using XRD, RAMAN and UV-Vis spectroscopy, SEM, FE-SEM, AFM, XPS and current – voltage measurement instruments.
- To fabricate field effect transistor (FET) using un-doped, Sn and Cu doped In$_2$O$_3$ thin films by the optimized method over silicon substrates. To study the characteristics of the FETs and the transistor parameters.
- To test the sensing behaviour of pure and doped In$_2$O$_3$ FETs with gases and to study the influence of the dopant concentration on sensing property.
- Substrate induced structure of In$_2$O$_3$ thin films has been tested with Si substrates and surface modified glass substrates. Its gas sensing properties were analyzed with ammonia, acetone and ethanol vapours.

1.6.2. The objectives of section B are:

- To prepare, characterize and optimize indium oxide nanoparticles using four different chemical methods.
- To analyze the structure, surface morphology, lattice parameter and composition of the prepared nanoparticles with XRD, RAMAN, SEM, FE-SEM, TEM/HR-STEM and EDX analysis.
- To synthesize thin films using the optimized nanoparticles and to use them as sensing elements to sense ethanol gas at room temperature.
Introduction

1.7. Organization of the work

This thesis is divided into nine chapters. The first chapter is of introductory nature. It gives an introduction to gas sensors, metal oxide sensors, FET sensors, the role of thin films and nanoparticles in the field of sensing etc. It gives a brief introduction to indium oxide and also includes a literature survey on indium oxide thin films and nanoparticles, doped indium oxide thin films and their gas sensing properties.

The second chapter deals with the preparation method adopted for the synthesis of undoped indium oxide thin films. The experimental details of the characterization techniques used to analyze the prepared thin films are discussed.

Preparation of Sn and Cu-doped indium oxide thin films are discussed in the third chapter. A detailed discussion on the results obtained from the different dopant concentrations and their influence on structural, surface, optical and electrical characteristics are also discussed. A compositional analysis (XPS) was also carried out to show the presence of the dopant and the conclusions obtained have been discussed.

A brief introduction about field effect transistors and the construction of FET from the prepared solutions over Si-SiO₂ substrates (both pure and doped indium oxide solutions) and their characteristics are discussed in the fourth chapter.

The fifth chapter deals with the field effect gas sensors and the constructed doped and undoped indium oxide field effect transistor sensor. Response of the FETs to different gases are plotted and discussed. Temperature dependent sensitivity and humidity cross response were analyzed and discussed.

The substrate effect of the method-I (dropped method) prepared coating solution was tested with Si-SiO₂ and surface modified glass substrates to observe any enhancement in the surface area of the films. The improvement in surface area has been analyzed using AFM measurements and the response to different gases was analyzed and the results are discussed in the sixth chapter.
Synthesis of indium oxide nanocubes using different methods is discussed in the seventh chapter. The results obtained from XRD, FE-SEM, TEM, EDX, Photoluminescence etc are discussed in this chapter. The optimization method and conditions are sorted out in the conclusion of the chapter.

The eighth chapter deals with the preparation of a composite film using optimized indium oxide nanocubes and Polyvinylalcohol (PVA). The prepared composite film’s surface has been analyzed using FE-SEM and AFM and the structure has been analyzed using XRD and Raman. Its sensing behaviour was tested with the reducing gas ethanol and the obtained results are discussed.

The last chapter summarizes the important conclusions drawn from the various investigations carried out on undoped, doped indium oxide thin films and FETs, indium oxide nanocubes and their sensing property in the form of composite films.

1.8. List of conferences, symposia, seminars and workshops

1.8.1. Papers presented in conferences

1. Nanostructured In$_2$O$_3$ Thin films – A simple Chemical Route
M.Seetha, S.Bharathi, D.Nataraj and D.Mangalaraj,

International Conference on Advanced Materials (ICAM-2008), organized by the school of chemical sciences, Mahatma Gandhi university, Kottayam, India, 18-21 February, 2008.

2. Synthesis of In$_2$O$_3$ Nanospheres and Nanocubes by precipitation method
M.Seetha, S.Bharathi, D.Mangalaraj and D.Nataraj.

International seminar on Mathematical and Experimental Physics, organized by PSGR Krishnammal College for Women, Coimbatore, India, 18-19 December, 2008.

3. Nanostructured Indium Oxide Thin film for the Detection of Reducing Gases

International Conference on Active/Smart Materials (ICASM-09), organized by Thiyagarajar College of Engineering, Madurai, India, 7 – 9 January, 2009.

(Won Best Oral Presentation Award)
4. Preparation Of Indium Oxide Nanoparticles From Aloe-Vera Plant Extract

M.Seetha, S.Bharathi, S.Rajagopal, D.Mangalaraj and D.Nataraj,

*International conference on nanomaterials and nanocomposites (ICNM-09),*

organized by Institute of Macromolecular Science and Engineering (IMSE), Kottayam, Kerala, India, 6-9 April, 2009.


M.Seetha, S.Bharathi, D.Mangalaraj and D.Nataraj,


*(Won Best Poster Presentation Award)*

6. Sn Doped In$_2$O$_3$ Nano-Grass on Glass Substrates: A New Approach Towards Room Temperature Gas Sensor

M.Seetha, N. Sabari Arul, D.Mangalaraj and P.C. Chen,


1.8.2. Papers published / communicated to journals

1) Optical investigations on indium oxide nano-particles prepared through precipitation method

M. Seetha, S. Bharathi, A. Dhayal Raj, D. Mangalaraj, D. Nataraj


2) Nanoporous indium oxide transistor sensor for the detection of ethanol vapours at room temperature

M. Seetha, A. Dhayal Raj, N. Sabari Arul, D. Mangalaraj

*Sensors and actuators B Chemical* (Under review)

3) Medium dependent size and shape tuning of Indium oxide nanocubes and its gas sensing properties

M. Seetha, D. Mangalaraj, Yoshitake Masuda

*Crystal Growth and Design* (Under review)
4) Polymer-embedded \(\text{In}_2\text{O}_3\) cubic crystals: Preparation and study on room temperature ethanol sensor

(to be communicated)

5) Cu doped \(\text{In}_2\text{O}_3\) thin film field effect transistor for sensing ethanol at room temperature

(to be communicated)
1.9. Reference


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