CHAPTER 3

MATERIALS AND METHODS

3.1 METAL OXIDE SEMICONDUCTORS

Transition metal oxides are a fascinating class of inorganic materials, exhibiting a wide variety of structures and properties. In metal oxide semiconductors (such as SnO$_2$, ZnO, WO$_3$, TiO$_2$ etc.), electrical conductivity changes depend upon the composition of the gas surrounding them. Therefore, they are the popular and useful sensing materials for making inexpensive gas sensing devices. Solid state gas sensors based on metal oxide semiconductors play a very important role in industrial safety, environmental monitoring, and process control due to their high sensitivity, stability and compatibility with microelectronic processes. Metal oxides with a large surface-to-volume ratio, having more active sites on their surfaces for physical or chemical interactions, have been reported for high performance gas sensors. Moreover, doping metal oxides with suitable promoters has been attracting considerable attention and is still a subject of extensive interest due to their great potential for addressing some basic issues about electronic transport phenomena as well as the related sensing applications. Oxide semiconductors are preferential in photo electrochemistry because of their exceptional stability against photo-corrosion on optical excitation in the band gap. Furthermore, the large band gap (>3 eV) of the oxide semiconductor is needed in DSSCs for the transparency of the semiconductor electrode for the
large part of the solar spectrum. Many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases. For instance all the following oxides show a gas response in their conductivity: Cr$_2$O$_3$, Mn$_2$O$_3$, Co$_3$O$_4$, NiO, CuO, CdO, MgO, SrO, BaO, In$_2$O$_3$, WO$_3$, TiO$_2$, V$_2$O$_5$, Fe$_2$O$_3$, GeO$_2$, Nb$_2$O$_5$, MoO$_3$, Ta$_2$O$_5$, La$_2$O$_3$, CeO$_2$ and Nd$_2$O$_3$. However, compared to the above mentioned metal oxides, the most commonly used material is SnO$_2$.

3.2 TIN DIOXIDE (SnO$_2$)

Tin dioxide (also called stannic oxide or tin oxide) semiconductor gas sensors were first proposed and patented in 1962 by Taguchi. Tin oxide (SnO$_2$) is a wide band gap ($E_g = 3.6$ eV) semiconductor. SnO$_2$ belongs to the important family of semiconductor oxide materials that combine low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum. These properties are sought after in a number of applications: notably as electrode materials in solar cells, light emitting diodes and flat panel displays. In addition, materials that change their properties depending on the ambient gas can be utilized as gas sensing materials. Although many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases, SnO$_2$ was one of the first considered and still is most the frequently used material for gas sensing applications. There is an obvious close relationship between the gas sensitivity of oxides and their surface chemical activity. Since nanostructure exhibits high surface to volume ratio, over the last several years, there have been considerable efforts to explore new routes to synthesize SnO$_2$ in several nanostructure forms.
Figure 3.1 The unit cell of the crystal structure of SnO\(_2\). Large circles indicate O atoms and the small circles indicate Sn atoms.

Tin dioxide, also known as stannic oxide, possesses the rutile structure, and it is the most abundant form of tin oxide. In addition to the common rutile (tetragonal) structured SnO\(_2\) phase, there also exists a slightly more dense orthorhombic high pressure phase. As a mineral, the stannic oxide is also called Cassiterite. Figure 3.1 shows the crystal structure of SnO\(_2\), wherein the tin atoms are six co-ordinates and the oxygen atoms are three co-ordinates. The lattice parameters are \(a = b = 4.737 \, \text{Å} \) and \(c = 3.185 \, \text{Å}\). The \(c/a\) ratio is 0.673. The ionic radii for O\(^{2-}\) and Sn\(^{4+}\) are 1.40 and 0.71 Å, respectively. The metal atoms (cations) are located at positions \((0, 0, 0)\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) in the unit cell and the O\(_2\) atoms (anions) at \(\pm (u, u, 0)\) and \(\pm (\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})\), where the internal parameter, \(u\), takes the value 0.307. Figure 3.1. The unit cell of the crystal structure of SnO\(_2\). Each cation has two anions at a distance of \(\sqrt{2}ua\) (2.053 Å) and four anions at \([2(\frac{1}{2}-u)^2+ (c/2a)^2]\) \(\frac{1}{2}\) a (2.597 Å). Its electrical conduction results from the existence of point defects (native and foreign atoms) which acts as donors and acceptors. Tin oxide is special in the respect that tin possesses a dual valency, with tin preferably attaining an oxidation state of 2\(^+\) or 4\(^+\). This dual valency facilitates a variation of the surface oxygen composition. The variation of surface
composition is instrumental in explaining and tailoring many of the unique chemical properties of the materials (Batzill & Diebold 2005). Tin oxide has a wide range of applications in low emission glass, electrodes, organic light emitting diodes optoelectronic devices, lithium batteries, gas sensors, heat reflectors and polymer based electronics (Parthibavarman, Vallalperuman & Sathishkumar et al 2014).

Moreover, SnO$_2$ has a lower cost when compared to actual available materials for similar applications. Nowadays, the research on these materials is focused to increase their photocatalytic properties in waste water treatment. One of the most common methods to modify the properties of metal oxides is introducing dopants. Band gap and the properties of nanomaterials can be improved by impurity doping. Doping introduces impurities into an extremely pure semiconductor for the purpose of modulating its electrical properties as well as catalyst. For example, for undoped semiconductor nanoparticles, a decrease in conductivity is expected due to the narrowing of valence and conduction bands resulting in an increase in energy gap (Louis Brus 1986). By adding impurity to pure semiconductors, the electrical conductivity may be varied by factors of thousands or millions. Transition metal (TM) doping has been proposed to introduce magnetic functionality in conventional semiconductors Dietl, Ohno & Matsukura et al (2000); Saito, Zayets & Yamagata et al (2003). There is a good correlation between the conduction band energy of wide band gap metal oxide semiconductor nanoparticles and adverse biological responses. Band gap is a major factor determining the electrical conductivity of a solid. A small band gap allows the solid to have a strong enough flow of electrons from the valence to conduction bands in order to have some conductivity. In general, the band gap increases with the decrease of particle sizes. Thus, band gap can be altered by reducing the crystal size to nanoscale. Now a days there are techniques available for reducing the crystal size to nanorange which are
known as nanocrystals. Preparation of these materials in the nanoscale with improved band gap is more useful due to the increased surface-to-volume ratio and improved efficiency as photocatalyst. TiO$_2$, SnO$_2$ and ZnO have been identified as dynamic photocatalysts for the degradation of several organic contaminants, synthetic dyes etc. due to non-toxic nature, low cost and chemical stability Lakshmi & Martin (1997).

3.3 APPLICATIONS OF SnO$_2$

- **Heterogeneous Catalysis**

Nanosized tin-oxide based catalysts exhibit good activity towards CO/O$_2$ reactions. As in most oxide catalysts, the oxidation reactions are supposed to follow the Mars-van Krevelen mechanism. In this mechanism, the molecules are oxidized by consuming lattice oxygen of the oxide catalyst which in turn is re-oxidized by gas-phase oxygen. This is possible because transition and post-transition oxides have multivalent oxidation states that allow the material to easily give up lattice oxygen to react with adsorbed molecules and can be subsequently re-oxidized by gas-phase oxygen. It is shown that for different oxygen chemical potentials, surfaces with Sn$^{4+}$ or Sn$^{2+}$ are stable. This indicates that an easy reduction and re-oxidation of SnO$_2$ surfaces can be expected in catalytic oxidation reactions. The role of many of these additives is not fully understood. Most of these additives are oxidized during operation conduction of the catalyst. A strong synergetic effect between the additives and SnO$_2$ is usually proposed that is manifesting itself in several ways. The special active site may be stabilized at the interface between the additives and SnO$_2$. 
Gas Sensors

Materials that change their properties depending on the ambient gas can be utilized as gas sensing materials. Usually, changes in the electrical conductance in responses to environmental gases are monitored. Tin oxide (SnO$_2$) has been investigated and used as a gas sensing material for numerous applications from the very start of the sensor industry. Millions of carbon monoxide (CO) alarms utilizing SnO$_2$ as the active sensing element have been produced and have demonstrated the long term (>10 years) dependable performance of tin dioxide sensors. In the past 15 years, considerable research has been conducted on understanding the chemical and electronic mechanisms that govern semiconductor sensor performance and on extending SnO$_2$ sensors to detection of other gases (H$_2$, acetone, methane, C$_2$H$_5$OH, etc.), including trace amounts of toxic gases (CO, H$_2$S, ozone, etc).

Environmental applications

One of the major environmental applications of nanotechnology is in the water treatment. 97% of the water on earth is salt water and can be used after desalination, but this involves expensive technologies. Carbon nanotube membranes prove to be economic due to reduced costs, improved ability to selectively remove contaminants, durability and size of the device. Similarly, nanofilters could be used to remediate ground water or surface water contaminated with chemicals and hazardous substances. Moreover, nanosensors could be developed to detect waterborne contaminants. Similar nanofilters and nanosensors are employed to check air pollution at very low concentrations. SnO$_2$ has the following environmental applications:
Photocatalytic degradation

Nanoscience and technology holds great potential for the continued improvement of technologies regarding environmental protection. Textile industries produce a large volume of colored dye effluents which are toxic and non-biodegradable (Freeman, Reife & Betowski 1998). These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Recently, there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes. AOPs include photocatalysis systems such as a combination of semiconductors and light and semiconductor and oxidants. Metal based semiconductor photocatalysts reveal good results than other techniques used in water treatment because of its high surface area. SnO$_2$ nanoparticles also show better physiochemical and catalytical properties (Shao, Dimitrov & Guan et al 2010). These may be used in future at large scale water purification. SnO$_2$ is known as one of the key functional material because of many active sites with high surface reactivity, the high absorption efficiency of light radiations and environmental safety with the wide range of applications in catalysis. Dyes can be degraded in the presence of photocatalyst upon irradiation with visible light because of their absorption in the visible region. A photocatalyst produces surface oxidation to eliminate bacteria and other materials when it is exposed to the sun or a fluorescent lamp. The high surface area to mass ratio of nanoparticles can greatly enhance the adsorption capacities of sorbent materials preventing the surface against corrosion. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites. This means that a given mass of material in nano form will be much more reactive than the same mass of material made up of larger particles.
Antibacterial applications

Nanoparticles have been successfully utilised in nano chemistry to enhance the activity of catalysts and their immobilization, in the semiconductor industry and in the field of medical and pharmaceutical sciences. The metal oxide nanomaterials show prominent antimicrobial properties. Metals such as silver, zinc and gold have been used for centuries as bactericidal and bacteriostatic agents each with different properties and spectrums of activity. There are many more metal oxide nanoparticles which exhibit antimicrobial properties (Stoimenov, Klinger & Marchin et al 2002). For example, nanoscale silver has antibacterial properties and is presently being used in consumer products such as socks, washing machines and bandages. The antibacterial activities of metals depend on their contact surface; a larger surface area of the nanoparticles allows a larger amount of interactions with other organic and inorganic molecules. The use of SnO$_2$ nanoparticles has been reported to enhance the antibacterial and anti-fungal effectiveness of Alovera extract (Ayeshamariam, Tajun Meera Begam & Jayachandran 2013).

3.4 CHEMICAL BATH DEPOSITION (CBD) METHOD

Basics of chemical bath deposition technique

Films can be grown on either metallic or nonmetallic substrates by dipping them in appropriate solutions of metal salts without the application of any electric field. Deposition may occur by homogeneous chemical reactions usual reduction of metal ions in solution by a reducing agent. If this occurs on a catalytic surface, it is called an electro less deposition (autocatalytic). Silvering is the most widely used for this technique, metallic as well as mixed film sulphides & selenides and other alloys can be deposited. For nonmetallic surfaces, a sensitizer has to be used. The growth rate & degree of crystallinity

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depends upon the temperature of the solution. The main advantage of this method is to deposit the films on non-accessible surfaces such as rounded glass tubes. The chemical bath deposition is the simplest of the chemical methods, and it has many advantages as;

1. It is simple & does not require any sophisticated instrumentation.
2. It is ideally suited for large area depositions & substrate surfaces of both accessible & no accessible nature could easily be deposited.
3. The deposition is usually at low temperature which avoids the oxidation or corrosion of the metallic substrates.
4. It is possible to obtain uniform & large area semiconductor deposits on a variety of substrate materials.
5. Thickness of the deposits can be controlled from few nanometers to micrometer by variation in the preparative parameters.
6. As compared to the other thin film deposition techniques, chemical bath deposition the process can be used conveniently for deposition of a variety of materials.

a) **Factors governing the chemical bath deposition**

It is the most suited method for deposition thin films. However, the growth of film is found to be governed by the various factors such as bath composition, the pH and deposition time & deposition temperature.
b) **Bath composition**

The growth rate and quality of the deposited films were greatly influenced by the concentration of the reacting species. The films deposited by using low concentration are thin and nonuniform. This observation relates to the insufficient supply of ionic species at such concentration levels. On the other hand when the concentration of the species was increased, the quality and uniformity of the films goes on increasing and the films can be thick. This is true up to a certain level of concentration and then saturation in the growth process was observed Figure 3.2.

![Figure 3.2 Schematic representation of chemical bath deposition method](image)

c) **The pH**

It is the most important factor in the chemical bath deposition. Thus, the desired films can be obtained on the substrate surface by optimizing the pH value of its bath solution which avoids the deleterious effects.
d) **Deposition time**

Growth of the thin film by chemical bath deposition is time dependent. The deposition time of the film affects film thickness.

e) **Deposition temperature**

The temperature dependence of growth rate is shown by literature survey that the rate of deposition increases with bath temperature resulting into the formation of fine grained structure.

### 3.5 SCOPE OF THE THESIS

The present work consists of the synthesis, characterization and a systematic investigation on the effect of metal ion dopants (Mg, Cu, W and Zr) on structural, optical and photocatalytic activities of SnO$_2$ nanostructured thin films. These materials were selected for the present study in view of their technological importance.

- The crystalline nature, phase purity, average crystalline sizes were analyzed by X-ray diffraction (XRD) technique.
- The functional groups of both pristine and doped SnO$_2$ were conformed through FT-IR and FT-Raman analysis.
- The surface topography and average particle size of the nanostructure films were observed by using AFM.
- The optical nature of the sample such as absorption, band gap energy was analyzed by UV-Vis transmittance spectroscopic technique.
- The oxygen deficiency and defects in crystals were analyzed by using photoluminescence study.

- The photocatalytic activities of the films were evaluated by degradation of methylene blue (MB) and rhodamine B (RHB) in an aqueous solution under ultraviolet light irradiation and to compare the efficiency of the catalyst with already existing reported values.