Chapter - 1

Introduction

1.1 Introduction to nanostructured metal oxides

Nanostructured materials have stimulated great interest in recent years due to their importance in basic scientific research and potential technological applications [Muhammed et al.(2003), Deven et al.(2012)]. They have become the focus of intensive research due to their unique properties and their potential for fabrication of high density nano-scale devices including sensors, electronic and optoelectronics. Because of their high surface to volume ratio and tunable electron transport properties, the electrical and optical properties of these materials are strongly influenced by minor perturbations. Therefore it is generally accepted that these materials are ideal systems for exploring a large number of novel phenomena and improved properties for advanced applications.

Among inorganic materials, nanostructured metal oxides have received intensive attention in diverse fields. The post transition metal oxides such as ZnO, In$_2$O$_3$, SnO$_2$, are one of the most important class of materials, with properties covering almost all aspects of materials science and solid state. These oxides are wide band gap semiconductors with high concentration of free electrons in their conduction band which arises either from defects in the materials or from extrinsic dopants. They exhibit metallic, semiconductor or insulator character due to the electronic structure difference and have unique physical, chemical, electrical and optical properties. The limited size in nanostructured metal oxides induces high density of corner or edge surface sites and brings about changes in conductivity and surface /chemical reactivity, which can be finally explored for different applications. Thus in the emerging field of nanotechnology a goal is to synthesize nanostructured metal oxides with highly improved properties with respect to those of bulk or single particle species.

A large number of methods based on solid, liquid and vapor phase growth of nanostructured metal oxides have been reported in literature. The most widely used methods include physical and chemical vapor deposition, laser ablation, hydrothermal process, chemical bath deposition, gel combustion, sol-gel process, electrochemical synthesis, solid state reaction and simple precipitation etc. [Liu et al.(2005), Jagdale et al.(2008), Mintz et al.(2005)].Template-assisted synthesis [Hulteen et al.(1997), Xue et al.(2005), Gang et
al. (2006)] has also been utilized for the growth of metal oxide nanostructures with well defined morphologies. Methods for preparation of nanocrystalline metal oxide films include spray pyrolysis, sputtering, thermal oxidation, spin coating, dip coating and many more. The nanostructures prepared by these techniques have shown to exhibit different properties owing to different dimensions and mirostructural set up and have been used in various applications such as as transparent conducting oxides (TCO) [Minami (2005)], oxidation catalysts [Weber et al. (2008)] and most importantly as solid state gas sensors [Vasiliev et al. (1998), Lu et al. (1998), Kim et al. (2000), Shinde et al. (2007), Chen et al. (2008)]. However development of simple and cost effective methodologies for synthesis of large-scale production of these nanoparticles remains a challenge. Therefore the main focus in present study is to review the recent progress in synthesis methodologies and establish a convenient route to prepare nanostructured semiconducting tin oxide that finds use in gas sensing applications.

1.2 General properties of Tin oxide (SnO$_2$)

SnO$_2$ is a transparent, n-type wide band gap semiconductor with its band gap typically reported as 3.6 eV or higher at 300K [Munnix et al. (1982)]. The presence of oxygen deficiency in the nominally pure material induces n-type conductivity which is attributed to the appearance of shallow donor levels at 0.03 and 0.15 eV below the conduction band. SnO$_2$ is of great interest due to its ability to tailor electrical and microstructural properties, making it useful in large number of applications such as varistors, catalysts, thick film resistors, and electrochemical devices such as gas sensors. Much of the ability to tailor SnO$_2$ properties comes from the multi-valence ability of the tin atom which allows for changes in the chemical behavior. These changes in the chemical behavior of SnO$_2$ can help to tune this material for specific applications.

1.2.1 Structure

SnO$_2$ crystallizes into a tetragonal rutile structure with space group D$_{4h}^{14}$ (P4$_2$/mmm). The unit cell of SnO$_2$ is shown in Figure 1.1. It consists of two Sn and four O atoms. Each Sn atom is surrounded by a distorted octahedron of six O atoms and each O atom has three nearest Sn neighbors at the corners of an almost equilateral tri-angle [Hartnagel et al. (1995)]. Thus it is a structure of 6:3 co-ordination. The lattice parameters of SnO$_2$ unit cell are $a = b = 4.731$ Å and $c = 3.189$ Å with c/a ratio of 0.673. The ionic radii for O$^{2-}$ and Sn$^{4+}$ are 1.40 and 0.71 Å, respectively.
Figure 1.1 Unit cell of SnO$_2$
1.3 Literature review

Achievement of nanostructured configurations of SnO$_2$ has gained due importance due to their unique properties. Consequently, in a short span of few years, SnO$_2$ nanostructures with different geometries namely nanowires, nanotubes, nanoribbons, nanodiskettes, nanoflakes, nanoplates and meso/nanoporous structures [Zheng et al.(2001), Dai et al.(2002), Dai et al.(2001), Hu et al.(2002), Wang et al. (2003), Sun et al.(2004), Xu et al.(2003), Wang et al.(2008), Ohgi et al.(2005), Pan et al. (2007), Toupance et al.(2003)] have been prepared using diverse techniques for different applications.

Yang et al.(2003) have reported the synthesis of nanosized SnO$_2$ powder by simple precipitation method. Photoluminiscence properties of SnO$_2$ nanoparticles synthesized by sol gel method have been studied by Gu et al.(2004). Kersen et al.(2006) have reported the synthesis of SnO$_2$, by high energy ball milling and different chemical reactions. These prepared nanoparticles have been used for H$_2$S sensing applications. Fan et al.(2006) have synthesized hollow nanospheres of SnO$_2$ by solvothermal method. A hydrothermal method has been used by Chiu et al.(2007) to prepare SnO$_2$ nanoparticles for sensing alcohols. Tien et al.(2008) have reported the synthesis of large area SnO$_2$ nanorods by pulse laser deposition. Hu et al.(2002) have synthesized SnO$_2$ nanoribbons by rapid oxidation of elemental tin. The strong photoluminescence of these synthesized nanoribbons in the visible region suggested their possible applications in nanoscale optoelectronic devices. A size controlled electrochemical synthesis of SnO$_2$ nanotubes has been proposed by Lai et al.(2009). The studies highlight that the length and diameter of the synthesized nanotubes can be controlled by deposition time. Shape selective synthesis of tin oxide has been studied by Ramgir et al.(2005) by employing RuO$_2$ as a promoter/nucleating agent. Monredon et al.(2012) have synthesized monodisperse spheroidal nanoparticles by hydrolysis of tin isopropoxide in the presence of acetylacetone and $p$-toluenesulfonic. These particles exhibited non aggregation due to protection by hybrid organic–inorganic layer containing acetylacetonate ligands, acetylacetone, $p$-toluenesulfonates and water.

Thin and thick films of nanostructured SnO$_2$ have been prepared both by physical and chemical deposition methods using variety of techniques. Giraldi et al.(2006) have reported the preparation of antimony (Sb) doped SnO$_2$ films by spin coating. These films display high transmittance of 80% in the visible range and also show good sensitivity towards NO$_x$ at high
operating temperatures. Jain et al. (2006) have prepared Ni and Al doped SnO$_2$ thick films by screen printing and studied the gas sensing parameters of the films. Serin et al. (2006) have reported the preparation of SnO$_2$ films by spray pyrolysis and studied their electrical, structural and optical properties. Thermally oxidized films of SnO$_2$ has been prepared by Partridge et al. (2008). Le et al. (2008) have reported the preparation of Sb doped SnO$_2$ films by sputtering at low temperatures and showed a significant improvement in the electrical and optical properties with oxygen concentration. Smith et al. (1995) have studied the effect of SnCl$_4$ and SnCl$_2$.2H$_2$O dissolved in methanol on the surface aspect and preferred orientation of SnO$_2$ films deposited by a pyrosol process. The studies show that molecules formed from SnCl$_4$ deposit more easily than polymer molecules produced from SnCl$_2$.2H$_2$O. Lee et al. (2006) have shown a change in preferred orientation of SnO$_2$ films by Sb doping. Luyo et al. (2007) have studied the influence of sol properties on the film morphologies and reported a stable and shorter gas sensing response of highly textured films. Studies on pure and aluminium doped SnO$_2$ films by Bhat et al. (2007) have shown that electron beam irradiation of the films brings about significant changes in the electrical and optical properties of films.

The conducted studies clearly demonstrate that reduced dimensionality, variations in process parameters with pre and post synthesis modifications cause a radical change in the properties of SnO$_2$ based nanomaterials that can be utilized for different applications.

1.3.1 SnO$_2$ as gas sensor

There is a great deal of interest in the development of gas sensors for application of air pollution monitoring, detection of harmful gases in mines, grading of agro-products like coffee and spices, home safety, exhaust gas monitoring, hand held breath analyzers etc. Some of the gases of interest are odorless and other gases cannot be detected by the nose at very low concentrations. It is therefore essential to monitor continuously the concentration of different hazardous gases and alarm if the gas concentration level is above a certain safety limit. Thus, there are enormous reasons that make the study and development of sensors an academically important issue. Materials which change their properties depending on the ambient gas can be utilized as gas sensing materials. Usually changes in the electrical conductance in response to gases are monitored.

For the last four decades several metal oxide based ceramic materials have been explored for gas sensing devices [Wang et al. (2010)]. Amongst all oxides, SnO$_2$ has been
widely accepted as an efficient gas sensing material. As compared to other gas sensing semiconductor oxides such as WO$_3$, TiO$_2$, ZnO, In$_2$O$_3$, Fe$_2$O$_3$, the high chemical activity of SnO$_2$ makes it highly sensitive to oxidizing and reducing gases even in their trace amounts. The conductivity of SnO$_2$ is very sensitive to the surface states in temperature range between 25 and 400°C due to the feasibility of redox reaction on its surface. Further the dispersing conduction band with its minimum at C-point and the high mobility of charge carriers in the material ensures that a change in charge carrier concentration due to the reactions results in a strong change in electrical conductance of the material [Mulla et al. (2004)]. As a result adsorbate induced band bending has the potential to result in strong conductivity changes in this material and thus triggers a stronger gas response signal. Besides this surface of tin oxide also exhibits good adsorption/desorption phenomenon and reactivity, mainly due to the availability of free electrons in its conduction band and the presence of surface and bulk oxygen vacancies and active chemisorbed oxygen.

SnO$_2$ nanostructures, because of their unique electrical properties are promising candidates towards miniaturized, ultra-sensitive chemical sensors [Gopel et al. (1995), Ansari et al. (1997), Nyaral et al. (1999), Scott et al. (2001), Leite et al. (2007)]. Nanostructured configurations of SnO$_2$ can be easily processed in powder and thin film forms and have shown promising properties in sensor application, especially low operating temperature, high sensitivity and thermal stability [Law et al. (2002), Wang et al. (2003), Maiti et al. (2003), Kolkamov et al. (2003)]. Pure and modified SnO$_2$ gas sensors prepared by different methods have been widely used for sensing large number of gases such as LPG, CH$_4$, CO, H$_2$, O$_2$, methanol, ethanol, ammonia, NO$_2$ etc. Malyshev and Pislyakov (2003) have developed SnO$_2$ thick-film semiconductor gas sensors, which were found to be highly efficient for detection of methane, hexane, hydrogen, carbon monoxide, ammonia, hydrogen sulphide and ethanol. LPG and Hydrogen sensing properties of nanostructured Rutherfordium doped tin oxide nanopowder have been studied by Niranjan et al. (2005). Carotta et al. (2008) have systematically studied the responses of alkanes to SnO$_2$-based materials with particular emphasis to the dehydrogenation mechanisms of surface reaction of these gases. Vaishampayan et al. (2008) have studied the response of pristine SnO$_2$ and Pd: SnO$_2$ towards different reducing gases. The 1.5-mol% Pd doped SnO$_2$ films showed improved response towards LPG at low operating temperature of 50°C. K. R. Han (2003) has worked on SnO$_2$ based gas sensors and found that
Fe$_2$O$_3$ was a more effective additive than Pd or Pt. It showed high response and high selectivity for H$_2$, CH$_4$, C$_4$H$_{10}$, and a little cross-sensitivity to ethanol and smoke. Wang et al. (2010) have studied ammonia sensing characteristics of nanocrystalline Sb doped SnO$_2$ synthesized by a non aqueous sol gel route. Rani et al. (2008) have reported an enhancement in ammonia sensitivity of SnO$_2$ films by irradiation of swift heavy Ni ions. A change in gas sensing behaviour from n to p type by irradiation has also been observed by them. Mesoporous structure and gas-sensing properties of SnO$_2$ powders prepared by utilizing the self-assembly of cationic surfactant have been studied by Hyodo et al. (2003). The effect of different metal and metal oxide additives on SnO$_2$ sensors have been studied by Yamazoe et al. (1983). Catalytic and gas sensing properties of SnO$_2$ are also found to be enhanced by growth of nanoparticles with exposed high energy facets. Wang et al. (2012) have reported a synthetic method for growth of octahedral SnO$_2$ nanoparticles enclosed by high energy $\{111\}$ facets. Use of tetramethyl ammonium hydroxide in the process has been found to be crucial for the control of exposed facets. The experiments demonstrated that these nanoparticles had highly enhanced catalytic activity and gas sensing properties. Han et al. (2012) have reported a hydrothermal route for synthesis of octahedral SnO$_2$ nanoparticles with high index $\{221\}$ facets. Gurlo (2007) has also discussed the effect of SnO$_2$ crystal size and shape on the gas sensing properties. The report suggests an important role of exposed high energy facets in enhancing the gas sensing properties.

SnO$_2$ thin films prepared by different techniques have been widely used for gas sensing applications. Korotcenkov et al. (2000) have studied the structural properties of SnO$_2$ films deposited by spray pyrolysis and have presented a detailed discussion on the influence of film deposition conditions on the structural and gas sensing properties. Brinzari et al. (2002) have also discussed the morphology and principle details of crystallographic grain structure of SnO$_2$ thin films prepared by spray pyrolysis. Niranjan et al. (2002) have developed a highly selective hydrocarbon sensor based on ruthenium doped SnO$_2$ thin films prepared by spray pyrolysis. Highly sensitive and quickly responding ultrasonically sprayed nanostructured SnO$_2$ thin films for hydrogen gas sensing have been developed by Patil et al. (2009).

The above studies on SnO$_2$ suggest that the material can be tailor made into a highly sensitive and selective sensor by judicious choice of operating temperature, microstructure and
modification by incorporation of additives, dopants, catalysts, promoters or by surface functionalization.

However inspite of the tremendous development and research on SnO$_2$ based gas sensors, the problems of high power consumption, low sensitivity, selectivity, stability, low speed of response etc are still persisting. So consistent efforts for development of highly efficient, low cost SnO$_2$ based materials for improved gas sensing applications are still going on. A recent trend indicates a more detailed study of SnO$_2$ base material from the point of view of improvising its performance through nanostructuring and material engineering, instead of continuing research for new materials for gas sensing applications. So in order to synthesize SnO$_2$ with specific properties for gas sensing applications it is important to envisage and develop efficient low cost synthesis strategies with a correct and necessary combination of methods of structural engineering for optimal result attainment.

1.4 Importance of the study

Keeping in view the above facts an attempt has been made to synthesize nanostructured SnO$_2$ powder and thin films by simple low cost synthesis techiques. The effect of different pre and post synthesis treatments on properties of synthesized materials has been investigated. The reaction conditions have been optimized in a systematic way to obtain samples with improved morphology and microstructure for gas sensing applications.

1.5 Objective of the Thesis

The objective of this research is to identify the conditions for the synthesis and development of SnO$_2$ based nanostructured materials capable of sensing small concentrations of oxidizing and reducing gases at low operating temperatures. In this context the present study focuses on the synthesis, characterization and gas sensing behaviour of nanostructured SnO$_2$ powders and thin films prepared by non aqueous sol gel and ultrasonic spray pyrolysis method. The samples have been prepared by the two techniques at different technological conditions and modifications which are supposed to result in the different structural, electrical, optical and gas sensing properties.
1.6 Framework of the thesis

The thesis has been divided into five chapters, the details of which are as under

Chapter-1 Introduction

This chapter begins with a general introduction to nanostructured materials with emphasis on metal oxide based nanostructures and their potential applications in different technological areas. A brief description of the structure and properties of SnO$_2$ along with a comprehensive review of literature on nanostructured SnO$_2$ and its gas sensing applications has been given. The main objective and framework of the thesis has been highlighted at the end of the chapter.

Chapter-2 Theoretical consideration

This chapter presents details on sol gel and spray pyrolysis technique for synthesis of nanostructured metal oxides. The basic principles of the techniques and their advantages over conventional methods have been discussed. The principle of gas detection and factors affecting the gas sensing response has been given. At the end a brief discussion on different technological methods used for modifying the synthesis and properties of SnO$_2$ based nanostructures have been presented.

Chapter-3 Experimental techniques

The details of chemicals and glassware used for the experiments, cleaning procedures, selection of precursors and various experimental conditions for synthesis of nanostructured SnO$_2$ by non aqueous sol gel and ultrasonic spray pyrolysis techniques are presented in this chapter. A brief description of various characterization techniques used to study the thermal, structural, optical and electrical properties of SnO$_2$ powder and thin film samples is also given. Description of the gas sensing set up and details of various sensing parameters are presented at the end of the chapter.

Chapter-4 Results and discussion

This chapter deals with the interpretation of results obtained from studies conducted on structural, optical, electrical and gas sensing properties of SnO$_2$ powder and thin films prepared by nonaqueous sol gel and ultrasonic spray pyrolysis techniques. The first section presents discussion on results obtained for SnO$_2$ powder samples calcined at different temperatures. The second part discusses the results for SnO$_2$ thin films deposited at different substrate temperatures, subjected to post deposition annealing and swift heavy ion irradiation.
The third part interprets the results obtained for surfactant assisted grown SnO$_2$ powder and thin film samples. The fourth section discusses the effect of Sb doping on SnO$_2$ powder and thin film properties.

**Chapter-5 Summary**

This chapter summarizes the results obtained on nanostructured SnO$_2$ powder and thin films prepared by non aqueous sol-gel and ultrasonic spray pyrolysis techniques.

**References**