CHAPTER 1

INTRODUCTION

1.1 TRANSPARENT CONDUCTING MATERIALS

Transparent conducting thin films are a class of materials which achieve large values of electrical conductivity while maintaining a high transmission in the visible range of the electromagnetic spectrum (Edwards et al 2004). Since the realisation of this type of materials, vast amounts of research and development have gone into commercialising these thin film coatings. The first transparent conducting oxide (TCO) material was reported in 1907 by K. Badeker. Badeker (1907) have prepared sputter coated a thin film of cadmium and heat treated the sample in air. The heating step led to the incomplete oxidation of the cadmium to non-stoichiometric cadmium oxide, leaving oxygen vacancies in its structure. The oxygen vacancies led to pentavalent cadmium ions, which generated occupied defect energy levels from which electronic promotion into the cadmium oxide conduction band could easily occur. Transparent conducting metal-oxides are the most common transparent conducting materials used, specifically tin doped indium oxide (ITO). This material is practical because it is extremely conductive, as well as being nearly transparent to visible light (>80%) when deposited as a thin film. Although ITO serves its purpose well as a transparent conducting material, the demand for ITO films has caused the price of indium to greatly increase. Although electronics recycling programs have reduced the price of indium in recent years, the demand is still increasing (Hosono 2012). Because
of this and because of other properties that may be desirable in the field of flexible electronics, alternative materials are being investigated. In order to be a successful transparent conducting material, there are many properties that the film must satisfy. Most importantly, the conductivity should be high and the visible light absorption coefficient should be low. There are other material-specific purposes that are important as well, such as flexibility, transparency to IR light and thermal stability. The current commercial products are based on n-doped metal oxide thin film, called transparent conducting oxides (TCO’s). These films have a far-reaching range of applications from heat-mirror window-coatings, which control the transmission of infrared energy into and out-of buildings (Gelin et al 2005), to their use as the transparent electrode materials in photovoltaic cells, touch-screen technology and flat panel displays including liquid crystal displays (LCD), organic light emitting displays (OLED) and plasma screen displays (Ginley 2000).

1.2 INTRODUCTION TO THIN FILMS

A material having one of its dimensions about one micron (or) less is the geometrical description of a thin film. Thin films have a very large surface to volume ratio and consequently the surface usually influences the properties of the film greatly. Because of compactness, better performance and reliability coupled with the low cost of production and low weight, thin film devices are preferred over their bulk counter parts. Thin film properties are largely dependent on the method of preparation.

The fact that the thin film science is possible is traced from the observations of Grove (Grove 1852) who noted that metal films were formed by sputtering of the cathode with high energy positive ions. Thin films are thin material layers ranging from fractions of a nanometer to several micrometers in thickness. Thin film materials are the key elements of
continued technological advances made in the fields of optoelectronic, photonic and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction. Some work is being done with ferromagnetic thin films as well for use as computer memory. Ceramic thin films are also in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for the protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools may extend the life of these items by several orders of magnitude. The engineering of thin films is complicated by the fact that their physics is in some cases not well understood. In particular, the problem of rewetting may be hard to solve, as there are ongoing debate and research into some processes by which this may occur. So a thin film is defined as a low dimensional material created by condensing, one by one, atomic/molecular/ionic species of matter. Thin film technology is a relatively young and growing ever field in the physical & chemical sciences which are a confluence of material science, surface science, applied physics and applied chemistry. Thin film technology has its objectives in the provision for scientific bases for the methods & materials used in thin film electronics. Thin films have a number of applications in various fields. Few of them are anti-reflection (AR) coatings, solar energy converters, transistors, coating technology, interference filters, polarizer’s, narrow band filters, solar cells, photoconductors, IR detectors, waveguide coatings, controlled aerospace devices and photo thermal solar coatings such as black Chrome, Nickel, Cobalt etc.
1.3 DEPOSITION TECHNIQUES FOR THIN FILMS

Thin film technology is one of the oldest arts and one of the newest sciences. Thin films have been used for more than half a century in making electronic devices, optical coatings, hard coatings, and decorative parts. A thin film has one of its linear dimensions very small compared to the other two and is characterized by a large surface to volume ratio. Any thin film deposition process involves the following sequential steps:

- Transition of the condensed phase (solid or liquid) into the gaseous state (atomic/molecular/ionic species)
- Transport of the vapour from the source to the substrate
- Condensation of the vapour upon arrival on the substrate

The deposition techniques are broadly classified into two - physical and chemical methods depending on how the atoms/molecules/ions/clusters of species are created for condensation process (George 1992). The physical method covers the deposition techniques, which depends on the evaporation or ejection of the material from a source, i.e. evaporation or sputtering, whereas chemical methods depend on physical properties. Structure-property relationships are the key features of such devices and basis of thin film technologies. Thus, chemical reactions may depend on thermal effects, as in vapour phase deposition and thermal growth. However, in all these cases a definite chemical reaction is required to obtain the final film. When one seeks to classify deposition of films by chemical methods, one finds that they can be classified into two classes. The first of these classes is concerned with the chemical formation of the film from the medium, and the typical methods involved are electroplating, chemical reduction plating and vapour phase deposition. A second class is that of the formation of this film from the precursor ingredients e.g. iodization, gaseous iodization, thermal growth,
sputtering ion beam implantation, CVD, MOCVD and vacuum evaporation. The methods summarized in Table 1.1 are often capable of producing films defined as thin films, i.e. 1 µm or less and films defined as thick films, i.e. 1 µm or more. However, there are certain techniques which are only capable of producing thick films and these include screen printing, glazing, electrophoretic deposition, flame spraying and painting. Here, we discuss some deposition techniques of thin films both physical and chemical deposition methods.

Table 1.1 Classification of thin film deposition techniques

1.3.1 Physical Techniques

i) Physical vapour deposition (PVD)

PVD processes proceed along the following sequence of steps:

a) The solid material to be deposited is physically converted to vapour phase,
b) The vapour phase is transported across a region of reduced pressure from the source to the substrate and

c) The vapour condenses on the substrate to
form the thin film. The conversion from solid to the vapour phase is done through physical dislodgement of surface atoms by the addition of heat in evaporation deposition or by momentum transfer in sputter deposition. The third category of PVD technique is the group of so-called augmented energy techniques including ion, plasma or laser assisted depositions (Mahan & John 2000).

ii) Evaporation

Evaporation or sublimation techniques are widely used for the preparation of thin layers. A very large number of materials can be evaporated and, if the evaporation is undertaken in vacuum system, the evaporation temperature will be very considerably reduced, the amount of impurities in the growing layer will be minimized. In order to evaporate materials in a vacuum, a vapour source is required that will support the evaporator and supply the heat of vaporization while allowing the charge of evaporator to reach a temperature sufficiently high to produce the desired vapour pressure, and hence the rate of evaporation, without reacting chemically with the evaporator. To avoid contamination of evaporate and hence of growing film, the support material itself must have a negligible vapour pressure and dissociation temperature of the operating (Mattox & Donald 2003).

iii) Sputtering

If a surface of the target material is bombarded with energetic particles, it is possible to cause ejection of the surface atom: this is the process known as sputtering. The ejected atoms can be condensed on to a substrate to form a thin film. This method has various advantages over normal evaporation techniques in which no container contamination will occur. It is also possible to deposit alloy films which retain the composition of the parent target material. DC sputtering, radio frequency sputtering and magnetron
sputtering methods are the oldest types of sputtering used. High-pressure oxygen sputtering and facing target sputtering are the two new methods introduced for deposition of thin films for applications in superconducting and magnetic films (Westwood & William 2003).

iv) **Ion plating**

In this atomistic essentially sputter-deposition process, the substrate is subjected to a flux of high energy ions, sufficient to cause appreciable sputtering before and during film deposition. The advantages of physical methods are laid in dry processing, high purity and cleanliness, compatibility with semiconductor integrated circuit processing and epitaxial film growth. However, there are certain disadvantages such as slow deposition rate, difficult stoichiometry control, high-temperature post deposition annealing often required for crystallization and high capital expenditure.

1.3.2 **Chemical and Electrochemical Techniques**

a) **Electro deposition**

It is a process of depositing a substance on the electrode by electrolysis, the chemical changes being brought about the passage of a current through an electrolyte. The electrode gains a certain charge on itself which attracts oppositely charged ions & molecules holding them at electrode / electrolyte interface. A double layer consisting of an inner layer of water molecules interposed by preferentially adsorbed ions & an outer layer of the charge opposite to that of the electrode is formed. During deposition ions reach, the electrode is formed. During deposition ions reach, the electrode surface stabilizes on it, release their ligands, release their charges and undergo electrochemical reaction. The rapid layer depletion of the depositing ions from the double layer is compensated by a continuous supply
of fresh ions from the bulk of the electrolyte. The factors influencing the electro deposition process are, i) current density, ii) bath composition, iii) pH of the electrolyte, iv) Temperature of the bath, v) agitation and vi) electrode shape (Christopher MA Brett & Ana Maria Oliveira Brett 1993).

b) **Spray pyrolysis**

This is a thermally stimulated reaction between the clusters of liquid vapour atoms of different spraying solutions of the desired compound onto a substrate maintained at elevated temperature. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal or cluster of crystallites of the product. The other volatile by-products and excess solvents escape in the vapour phase. The thermal energy for decomposition, subsequent recombination of the species, sintering & recrystallisation of the crystallites is proved by a hot substrate. The nature of the fine spray droplets, with the help of a carrier gas, depends upon spray nozzle. The growth of a film by a spray pyrolysis is determined by the nature of the substrate, solution as well as spray parameters. The films are generally strong and adherent, mechanically hard, pinhole free & stable with temperature and time. The morphology of the films is generally rough and that will depend upon the spray conditions. The surface of the substrate gets affected in the spray process and the choice is limited to glass, quartz, ceramics or oxides, nitride or carbide coated substrates.

c) **Chemical vapour deposition (CVD)**

Chemical vapour deposition can be defined as a material synthesis method in which the constituents of vapour phase react to form a solid film at the surface. The chemical reaction is an essential characteristic of this method; therefore, besides the control of the usual deposition process variables, the reactions of the reactants must be well understood. Various
types of chemical reactions are utilized in CVD for the formations of solids are pyrolysis, reduction, oxidation, hydrolysis, synthetic chemical transport reaction etc.

d) Cathodic deposition

This is a standard method of electroplating. Two metal electrodes are dipped into an electrolyte solution and on the application of an external field across the electrodes; metal ions from the solution are deposited on the cathode as a film. Deposition of the films is mainly controlled by the electrical parameters such as electrode potential and current density.

e) Anodic oxidation

This is an electrolytic method for producing oxide films on the surface of metals. These metals form the anode that dips into a liquid electrolyte such as a salt and acid solution. Oxide ions are attracted to the anode to form a thin layer of metal oxide. On increasing the field strength, more oxide ions diffuse through the oxide layer to the metal surface and, hence, the oxide layer grows thicker.

1.4 APPLICATIONS OF THIN FILMS

Although the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of micro miniaturization made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high-density storage techniques and it is this which has stimulated most of the research on the magnetic properties of thin films. Many thin film devices have been developed which have found themselves looking for an application or,
perhaps more importantly market. In general these devices have resulted from research into the physical properties of thin films. Secondly to generate ideas for new devices, fundamental research has led to a dramatic improvement in understanding of thin films and surfaces. This, in turn, has resulted in a greater ability to fabricate devices with predictable, controllable and reproducible properties. The cleanliness and nature of the substrate, the deposition conditions, post-deposition heat treatment and passivation are vital process variables in thin film fabrication. Therefore, prior to this improvement in our understanding of thin films, it had not really been possible to apply them to real devices. Thirdly, much of the finance for early thin film research originated from space and defence programmes to which the device cost is less important than its lightweight and other advantages, the major applications of thin film technology are not now exclusively in these areas but rather often lie in the domestic sector in which low cost is essential. Thin film materials have already been used in semiconductor devices, wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs, electro-optic coatings, memories, multilayer capacitors, flat-panel displays, smart windows, computer chips, magneto-optic discs, lithography, micro electromechanical systems (MEMS) and multifunctional emerging coatings, as well as other emerging cutting technologies (Mohan 1994).

i) Optical coatings

An optical coating is one or more thin layers of material deposited on an optical component such as a lens or mirror, which alters the way in which the optic reflects and transmits light. One type of optical coating is an antireflection coating, which reduces unwanted reflections from surfaces and is commonly used on spectacle and photographic lenses. Another type is the
high-reflector coating which can be used to produce mirrors which reflect greater than 99.99% of the light which falls on them. More complex optical coatings exhibit high reflection over some range of wavelengths, and anti-reflection over another range, allowing the production of dichroic thin-film optical filters.

ii) Photovoltaic

In the familiar rigid solar panel, the energy of incoming photons is converted to electricity in cells containing two thin layers of crystalline silicon. What makes a roll-to-roll production of flexible film solar products possible is the replacement of crystalline silicon with amorphous silicon, supplied in high-solids slurries that can be deposited onto substrates by web-converting processes like slot die coating. Microlayer film, Extrusion Dies Industries (EDI) can outfit its contour cast film dies with a new system, based on technology licensed from ‘The Dow Chemical Company’, which makes it possible to produce film of standard thickness, applications, which require barrier layers to prevent performance multiple layer-to-layer interfaces create a torturous path for gas molecules and thus substantially increase the barrier properties of the film. This is critical for photovoltaic applications, which require barrier layers to prevent performance losses caused by infiltration of oxygen or moisture vapour. Many in the solar power industry and the investment community believe the arrival of grid parity, the point when cost of electricity generated by a rooftop photovoltaic (PV) cell system is equivalent to that purchased from an electrical utility will mark a major inflection point for the market that will deliver a huge increase in growth. However, even when true grid parity arrives, it’s unlikely to generate an abrupt rise in solar system installations due to the high upfront costs and the long-term return of investing in a rooftop photovoltaic system, according to iSuppli Corp. In fact, growth is set to moderate during the years when grid
parity arrives for various regions of the world as the industry enters a more mature phase.

iii) **Semiconductor**

   Historically, the semiconductor industry has relied on flat, two-dimensional chips upon which to grow and etch the thin films of material that become electronic circuits for computers and other electronic devices. This thin layer (only a couple of hundred nanometers thick) can be transferred to glass, plastic or other flexible materials, opening a wide range of possibilities for flexible electronics. In addition, the semiconductor film can be flipped as it is transferred to its new substrate, making its other side available for more components. This doubles the possible number of devices that can be placed on the film. By repeating the process, layers of double-sided, thin-film semiconductors can be stacked together, creating powerful, low-power, three-dimensional electronic devices. Germanium has a much higher adsorption for light than silicon. By including the germanium without destroying the quality of the material, we can achieve devices with two to three orders of magnitude more sensitivity. That increased sensitivity could be applied to create superior low-light cameras or smaller cameras with greater resolution.

iv) **Photo electrochemical cells (PECs)**

   In photo electrochemical cells (PECs) experiments, irradiation of an electrode with light that is absorbed by the electrode material causes the production of a current (a photocurrent). The dependence of the photocurrent on the wavelength, electrode potential, and solution composition provides information about the nature of the photo process, its energetic, and its kinetics. Photocurrents at electrodes can also arise because of photolytic processes occurring in the solution near the electrode surface. Photo
electrochemical studies are frequently carried out to obtain a better understanding of the nature of the electrode-solution interface. Photo electrochemistry and electro generated chemiluminescence photocurrent can represent the conversion of light energy to electrical and chemical energy; such processes are also investigated for their potential practical applications. Since most of the studied photo electrochemical reactions occur at semiconductor electrodes, we will review briefly the nature of semiconductors and their interfaces with solutions. Consideration of semiconductor electrodes also helps in gaining a microscopic understanding of electron-transfer processes at solid-solution interfaces.

v) Optoelectronic

An optoelectronic thin-film chip, comprising at least one radiation-emitting region in an active zone of a thin-film layer and a lens disposed downstream of the radiation-emitting region, the said lens being formed by at least one partial region of the thin-film layer, the lateral extent of the lens being greater than the lateral extent of the radiation-emitting region. The thin-film layer is provided for example by a layer sequence which is deposited epitaxially on a growth substrate and from which the growth substrate is at least partly removed. That is to say that the thickness of the substrate is reduced. In other words, the substrate is thinned. It is furthermore possible for the entire growth substrate to be removed from the thin-film layer. The thin-film layer has at least one active zone suitable for generating electromagnetic radiation. The active zone may be provided for example by a layer or layer sequence which has a p-n junction, a double heterostructure, a single quantum well structure or a multiple quantum well structure. Preferably, the active zone has at least one radiation-emitting region. In this case, the radiation-emitting region is formed for example by a partial region.
of the active zone. Electromagnetic radiation is generated in the said partial region of the active zone during operation of the optoelectronic thin-film chip.

vi) Data storage

As the data storage density in cutting edge microelectronic devices continues to increase, the super paramagnetic effect poses a problem for magnetic data storage media. One strategy for overcoming this obstacle is the use of thermo mechanical data storage technology. In this approach, data is written by a nanoscale mechanical probe as an indentation on a surface, read by a transducer built into the probe, and then erased by the application of heat. An example of such a device is the IBM millipede, which uses a polymer thin film as the data storage medium. It is also possible; however, to use other kinds of media for thermo mechanical data storage, and in the following work, we explore the possibility of using thin film Ni-Ti shape memory alloy (SMA). Previous work has shown that nanometer-scale indentations made in martensite phase Ni-Ti SMA thin films recover substantially upon heating. Issues such as repeated thermo-mechanical cycling of indentations, indent proximity, and film thickness impact the practicability of this technique. While there are still problems to be solved, the experimental evidence and theoretical predictions show SMA thin films are an appropriate medium for thermomechanical data storage.

vii) Gas Sensors

Advancements in micro technology and the evolution of new nonmaterial and devices have been playing a key role in the development of very accurate and reliable sensors. The technology of sensors has developed tremendously in the last few years owning to many scientific achievements from various experiments, offering newer challenges and opportunity to the quest for every smaller devices capable of molecular level imaging and
monitoring of pathological samples and the macromolecules has lately gained the focus of attention of the scientific community, particularly for remote monitoring due to the increasing need for environmental safety and health monitoring. Gas sensors generally operate different principles and various gas sensing elements have been developed during the past years, out of which resistive metal oxide sensors comprise a significant part.

1.5 REVIEW OF PREVIOUS WORKS

In (Bauer 1937) prepared first SnO$_2$ semiconductor thin films by heating a thin film deposited on a quartz substrate in an oxygen atmosphere. Jarzabski and Marton (Bosnell & Weghorne (1973) have brought out an excellent review article summarizing the optoelectronic properties of SnO$_2$. Magnesium (Mg) doped SnO$_2$ polycrystalline thin films are deposited by Spray pyrolysis method (Boben Thomas & Benoy Skariah 2015). Mg doping significantly modifies the gas sensing properties of tin oxide thin films by yielding (1 1 0) and (1 0 1) crystallite orientation to accommodate oxygen vacancies which lead to enhanced oxygen adsorption. The structure, surface chemical composition, and the optical and electrical properties are studied in relation to the gas sensing magnitude. It is shown that the magnesium doping in SnO$_2$ maintains tetragonal rutile structure in stable cassiterite phase over low doping concentrations, which is confirmed by XRD analysis. The grain dimensions are influenced by both doping concentration and substrate temperature. Electronic surface states identified by the XPS are deconvoluted to establish the constituent oxygen states while the Energy dispersive spectra (EDS) compositional analysis indicates added oxygen adsorption. The sensor response to LPG is improved significantly (93%) by the addition of minor amounts of Mg to SnO$_2$ thin film sensors.

Zhang Tao, Zhang Tonghe & Chen Jun et al (1997) have prepared Implantation of Mg and Nb ions into 300 nm thick SnO$_2$ thin films, which
were deposited on Si wafers by Ar ion sputtering SnO\textsubscript{2} targets. The as-prepared films were subjected to annealing in an air atmosphere at 500°C for 2 hours. XRD and XPS analyses of films were conducted. It was found that Mg implantation prevented grains of SnO\textsubscript{2} thin films from growing in subsequent annealing, and conversely for Nb implantation. Matei Ghimbeu, Van Landschoot & Schoonman et al (2007) have successfully synthesized tin (IV) oxide thin films were deposited on platinum-coated alumina substrates by means of electrostatic spray deposition (ESD) technique using as precursor solution tin chloride pentahydrate (SnCl\textsubscript{4}.5H\textsubscript{2}O) in ethanol. The influence of the deposition parameters (temperature, time and flow rate) and copper addition on the morphology and microstructure of the films was studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy, respectively. The tetragonal rutile phase is evidenced by X-ray diffraction (XRD) with no other phases observed. The size of the particles calculated from the XRD peaks are in the nanometer range (7–10 nm) which is in good agreement with the TEM results. The Raman spectra indeed have revealed that the SnO\textsubscript{2} films are crystallized in the rutile tetragonal phase and furthermore a peak shift and a decrease of the peaks intensity can be remarked for the films doped with CuO.

Sb-doped and Cu-doped SnO\textsubscript{2} thin films were deposited by the photochemical method by (Dengbaoleer Ao & Masaya Ichimura 2012). A solution containing SnSO\textsubscript{4} and a doping solution containing SbCl\textsubscript{3} or CuSO\textsubscript{4} were alternately dropped on the glass substrate and irradiated by the UV light. The Auger electron spectroscopy measurement revealed that Sb or Cu was contained in the deposited thin films. The dependence of electrical properties of the films on annealing temperature was studied. The Cu-doped SnO\textsubscript{2} thin film showed enhanced electrical conductivity after 400°C annealing in a nitrogen atmosphere. Camelia Matei Ghimbeu, Martine Lumbreras &
Maryam Siadat et al (2008) have reported electrostatically sprayed tin oxide (SnO$_2$) and tin oxide doped with copper oxide (1, 2, and 4 at.% Cu) films to detect different pollutant gases, i.e., H$_2$S, SO$_2$, and NO$_2$. The influence of a copper oxide dopant on the SnO$_2$ morphology is studied using scanning electron microscopy (SEM) technique, which reveals a small decrease in the porosity and particle size when the amount of dopant is increased. The sensing properties of the SnO$_2$ films are greatly improved by doping, i.e., the Cu-doped SnO$_2$ films have large response to low concentration (10 ppm) of H$_2$S at low operating temperature (100°C). Furthermore, no cross-sensitivity to 1 ppm NO$_2$ and 20 ppm SO$_2$ is observed. Among the studied films, the 1 at.% Cu-doped SnO$_2$ layer is the most sensitive in the detection of all the studied gases.

Mi Wang, Yanfeng Gao & Zhang Chen et al (2013) have prepared high-quality transparent and conductive tungsten-doped tin oxide (SnO$_2$:W) thin films with different thickness (from 60 to 600 ± 10 nm) were fabricated on quartz glass substrates by a solution-based method. A stable solution was prepared from tin chloride and ammonium tungstate together with polyvinyl alcohol as a film-forming promoter. It was found that all films showed homogeneous composition, smooth surface with no cracks and high transparency with the optical band gap ranging from 3.93 to 4.31 eV. The effect of tungsten concentration, spin rate and annealing temperature on the morphological, electrical and optical properties of the films has been investigated. W doping has a large influence on the microstructure and the conductivity of the SnO$_2$ thin films. The lowest resistivity of $2.8 \times 10^{-3}$ $\Omega$ cm was obtained for a SnO$_2$: 3 at% W film, which was prepared at 3000 rpm and annealed at 800°C in air. An eight-layer film with a sheet resistance of 60 $\Omega$/sq and a thickness of 606 nm could be fabricated by multiple coating operation, which still exhibited an optical transmittance of over 80% in the visible region from 400 to 700 nm.
The influence of Cu doping on electro-physical, structural and gas sensing properties of the SnO$_2$ films were deposited by spray pyrolysis method (Korotcenkov, Boris & Cho 2013). It was shown that the addition of Cu in SnO$_2$ even in small concentrations was accompanied by strong changes in the SnO$_2$-based gas sensors performances. The reasons of observed changes were discussed. The conclusion was made that the decrease of response of heavy doped SnO$_2$:Cu-based gas sensors was mainly connected with both structural disordering of heavy doped SnO$_2$:Cu metal oxide and the appearance of the finely dispersed phase formed in the SnO$_2$ matrix. Yanwei Huang, Guifeng Li & Jiahan Feng et al (2010) have prepared tungsten-doped tin oxide (SnO$_2$:W) and transparent conductive films were prepared on quartz substrates by pulsed plasma deposition method with a post-annealing. The structure, chemical states, electrical and optical properties of the films have been investigated with tungsten-doping content and annealing temperature. The lowest resistivity of $6.67 \times 10^{-4}$ Ω cm was obtained, with carrier mobility of $65 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and carrier concentration of $1.44 \times 10^{20} \text{ cm}^{-3}$ in 3 wt.% tungsten doping films annealed at 800°C in air. The average optical transmittance achieves 86% in the visible region, and approximately 85% in the near-infrared region, with the optical band gap ranging from 4.05 eV to 4.22 eV.

The effects of W doping on the characteristically properties of SnO$_2$ thin films prepared by sol–gel spin coating method were investigated (Eyüp Fahri Keskenler, Güven Turgut & Serdar Aydin et al 2013). The SnO$_2$ thin films were deposited at various W doping ratios and characterized by various measurements. XRD studies indicated that the undoped and W doped SnO$_2$ films had cubic and tetragonal phases. The SEM images of WTO thin films showed cubic shaped nanocubes corresponding to cubic phase and the smaller particles corresponding to tetragonal phase were formed on the film surfaces, and their distributions and sizes were dependent on the W doping.
ratio. EDX spectroscopy analyses showed that the calculated and participated atomic ratios of W/(W + Sn) (at.%) in the starting solution and in the WTO thin films were almost close. It was found that the sheet resistance depended on W doping ratio and 2.0 at.% W doped SnO$_2$ (WTO) exhibited the lowest value of sheet resistance ($7.11 \times 10^3 \Omega/$cm$^2$). Anjali Sharma, Monika Tomar & Vinay Gupta (2012) have reported highly sensitive and novel sensor structure comprising of SnO$_2$ film and WO$_3$ micro-discs has been developed for trace level detection of NO$_2$ gas at lower operating temperature. Loading of WO$_3$ on SnO$_2$ film surface in the form of uniformly distributed micro-discs (8 nm thin, 600 µm dia.) was found to enhance the sensing response ($5.4 \times 10^4$) with fast response speed (67 s) at 100°C. Spill over of NO$_2$ gas molecules by WO$_3$ micro-discs on the uncovered surface of SnO$_2$ film and subsequently its reaction kinetics at Sn and W sites could be responsible for modulation of depletion width at n–n semiconductor heterojunction and may play an important role in enhanced response characteristics.

Thin SnO$_2$ films doped with Zr and Pd are obtained by the spray-pyrolysis method. The films are sensitive to 0.1 ppm phosphine at an operating temperature of 250–400°C. The sensitivity, response and recovery time are studied as a function of the Zr concentration. The chemical and phase compositions and microstructure of the films obtained are investigated by EDX, XRD and SEM analysis. The strong influence of Zr on the microstructure and gas-sensing characteristics of the films has been established Ratcheva, Stambolova & Konstantinov (1994). The effect of zirconia additions on sintering of CoO doped tin dioxide has been investigated by Mâitre, Beyssen & Podor (2004). A first study showed that the substitution of tin by zirconium reduces significantly the volatilization rate of SnO$_2$ for temperatures greater than 1400°C. It appeared that the zirconium content increase inhibits the densification kinetics of SnO$_2$-based ceramics. Indeed, the relative density did not exceed 93% for a Zr content lower than
6 mol% in the Sn(1–x)ZrxO2 solid solution. This negative effect can be imputed to the elastic distortions caused by the introduction of Zr in the tin dioxide lattice. So, the diffusion rate of point defects such as oxygen or cobalt ions is lowered.

Thin-film transistors (TFTs) with zirconium-doped tin oxide (ZSO) channels were fabricated by co-sputtering Sn and Zr metal targets (Dong-Suk Han, Jae-Hyung Park & Yu-Jin Kang et al 2013). The effect of Zr on the performance of SnOx-based TFTs was studied. TFTs with an intrinsic SnOx channel did not show promising performance. However, ZSO TFTs exhibited improved electrical properties, with increased ION/IOFF and decreased subthreshold swing. The influence of zirconium doping on bias stability in tin oxide TFTs was also investigated. ZSO TFTs exhibited turn-on voltage (VON) shifts of +9 V for positive stress bias, compared with +18 V for intrinsic SnOx TFTs. The improvements in device performance and stability were attributed to reduced carrier concentration induced by carrier trapping at Zr impurity sites.

The microstructure of M-doped SnO2 (M = Cr3+, Cu2+ and Pd2+) prepared by the sol–gel method and their gas-sensing performance were investigated (Wen Zeng, Tianmo Liu & DeJun Liu et al 2011). In particular, we focus on the effects of metallic ions on the hydrogen sensing behavior of the SnO2-based sensor. It is found that hydrogen gas response of SnO2 can be enhanced evidently by adding Pd2+ while such effect from Cr3+ and Cu2+ exhibits somewhat slight. A theoretical study based on first principles calculation shows that SnO2–Pd (1 1 0) surface enable adsorb more H2 gas and receive larger electrons from adsorbed H2 molecule, thereby holding the potential for the improvement of gas response to hydrogen. Sahana, Sudakar & Dixit et al (2012) have prepared nanocrystal formation of SnO2 in xSnO2–(100 – x) MgO (x in mol.%) nanocrystalline composite thin
films. SnO$_2$ and MgO exhibit strong immiscibility behavior below 750°C, leading to a controllable particle size of SnO$_2$ in the MgO matrix by changing their composition. The particle size of SnO$_2$ can also be controlled by increasing the annealing temperature. Above 750°C MgO and SnO$_2$ react to yield a MgO–Mg$_2$SnO$_4$–SnO$_2$ composite in which the size of the SnO$_2$ nanophase increases with the increase in temperature. By controlled choice of the composition and annealing conditions, the band gap of SnO$_2$ can be continuously increased from 3.89 to 4.5 eV. This behavior discuss in terms of the quantum confinement effect. The method provides a generic approach to tuning the band gap in nanocomposite systems over a wide energy range.

Magnesium oxide-coated tin oxide aggregates were prepared by a facile method (Shengjun Li, Zeng Chen & Tao Li et al 2014). The aggregates consisted of nanoparticles which provided a large surface area of 74.27 m$^2$ g$^{-1}$. Crack-free MgO-coated SnO$_2$ porous films were prepared using electrophoretic deposition method. The causes which prevent the forming of cracks were also discussed. For the application in dye-sensitized solar cells, the electrophoresis conditions, such as the amount of MgO loading and deposition duration, were optimized. The MgO-coated SnO$_2$ photo anode showed excellent photovoltaic response in the long wavelength region between 550 nm and 700 nm. The optimized MgO-coated SnO$_2$ photo anode showed an overall power conversion efficiency above 7.0% under AM 1.5G illumination (100 mW cm$^{-2}$) having a short circuit current density, open circuit voltage and fill factor of 20.0 mA cm$^{-2}$, 0.618 V and 0.57, respectively. Single-phase polycrystalline magnesium-doped tin oxide (Mg$_x$Sn$_{1-x}$O; x=0, 0.04 and 0.08) thin films were deposited by electron beam evaporation on the glass substrate (Syed Mansoor Ali, Syed Tajammul Hussain & Jan Muhammad et al 2013). X-ray diffraction analysis showed that the peaks intensity of the polycrystalline $\alpha$-SnO thin films increased along with the increase of Mg content. The crystallite size calculated from X-ray
diffraction data decreased by the increase of the Mg doping concentration, which was also confirmed by atomic force microscopy. The stoichiometry and thickness of the thin films were determined by Rutherford backscattering spectroscopy. An increase in both the optical transmission (57–95%) and band gap (2.5–2.82 eV) of the Mg$_x$Sn$_{1-x}$O thin films were observed which were investigated by UV–Vis spectroscopy. Photoluminescence of Mg$_x$Sn$_{1-x}$O thin films revealed that there were two extra peaks at 482 nm and 550 nm due to the crystal defects introduced by the Mg doping and these peaks became weaker and shifted to longer wavelength by increasing the Mg doping concentration.

Haiying He, Zhengcai Xie & Qingqing Li et al (2015) have investigated the nanocrystalline powders of MgO–SnO$_2$ (MgSnO) were experimentally obtained via a high-energy ball milling process with various operating time and annealing temperatures. The average crystallite size and lattice strain of the MgSnO powder decreased and increased, respectively, with the increase of milling time. The x-ray diffraction results revealed that the Mg$_2$SnO$_4$ phase formed after calcination of the as-milled MgSnO powder at temperatures higher than 1000°C. The film annealed at 500°C exhibited a much higher transmittance (~92%) in the visible region than that of a previously reported, non-ball-milled Mg-doped SnO$_2$. The surface morphology of MTO films is dependent on the annealing temperature. The fabricated MgSnO TFT operating in electron-accumulation mode can perform n-channel operations. In addition, the sub-threshold voltage swing value of the device is 0.29 V/decade. The gas sensitivity of SnO$_2$-based thin films doped with 0.05–2wt.% Cu has been reported Niranjan, Patil & Sainkaret et al (2003). The films were deposited by the conventional spray pyrolysis technique. The H$_2$S sensitivity and selectivity in relation to the concentration of Cu in SnO$_2$ has been systematically studied. A remarkable sensitivity towards H$_2$S at the operating temperature of 200°C is observed for
the Cu-doped SnO$_2$. The incorporation of Cu in the SnO$_2$ makes the film crystalline at lower deposition temperatures along with an enhanced sensitivity towards H$_2$S. The 1.19 wt.% Cu-doped SnO$_2$ exhibits a sensitivity of 910 for H$_2$S as compared to 12 for the pure SnO$_2$ at an operating temperature of 200°C, where the sensitivity of the film is calculated as the ratio of change in the conductance to the original conductance. The effect of surface coverage, morphology, oxidation state and the amount of Cu on the sensitivity has been studied. The correlation between Cu incorporation in the SnO$_2$ thin film at different deposition temperatures and the improvement in the selectivity and sensitivity towards hydrogen sulfide is discussed.

Ning Wan, Ping Yu & Shuwei Sun et al (2014) have reported Cu-doped SnO$_2$ (Cu/SnO$_2$), Cu and N co-doped SnO$_2$ (Cu–N/SnO$_2$) and to modify the electrochemical properties of SnO$_2$. The phase structure, component, morphology and chemical environment of as-prepared samples are extensively investigated. It is found that doping and a co-doping process does not affect the bulk structure of pristine SnO$_2$. Galvanostatic cycling indicates that the Cu–N/SnO$_2$ hierarchical microspheres exhibit much improved electrochemical stability. Further cyclic voltammetry (CV) analysis shows that Cu and N co-doping accelerates the electrode reaction. Hydrogen sulphide (H$_2$S) sensors, exhibiting high sensitivity (>10$^4$ in 50 ppm of H$_2$S) and short response time (80s), have been developed employing tin oxide:copper oxide (SnO$_2$:CuO) composite thin films (Katti, Debnath & Muthe et al 2003). The films were prepared by thermal evaporation of Sn and Cu metals on recrystallized alumina substrates, followed by oxidation at high temperatures. Results of various studies, such as scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS) reveal that SnO$_2$ and CuO are mutually non-reactive. The CuO grains, which in turn reside in the inter-granular regions of SnO$_2$, inhibit grain growth of SnO$_2$ as well as form a network of p–n junctions. Results of
XPS measurements revealed that the formation of Cu(OH)$_2$ due interaction of sensor film with ambient moisture causes drifts in sensor characteristics (low sensitivity and slow response) on prolonged operation in the industrial environment. The sensitivity and response time of degraded sensors could be restored either by exposing the sensor to a high H$_2$S dose (>100 ppm) or by heating it to an elevated temperature (>400 °C).

Yanwei Huang, Qun Zhang & Guifeng Li et al (2009) have prepared transparent conductive oxide tungsten-doped tin oxide thin films were deposited on glass substrates from ceramic targets by the pulsed plasma deposition method. The structural, electrical and optical properties have been investigated as functions of tungsten doping content and oxygen partial pressure. The lowest resistivity of 2.1×10$^{-3}$ Ω·cm was reproducibly obtained, with carrier mobility of 30 cm$^2$V$^{-1}$s$^{-1}$ and carrier concentration of 9.6×10$^{19}$ cm$^{-3}$ at the oxygen partial pressure of 1.8 Pa. The average optical transmission was in excess of 80% in the visible region from 400 to 700 nm, with the optical band gap ranging from 3.91 to 4.02 eV. Thin copper-doped SnO$_2$ films have been shown to exhibit sensitivity to PH$_3$ in the region of its threshold limit concentrations in air. The films were deposited by spraying alcohol solutions of SnCl$_4$ and CuCl$_2$ over hot quartz substrates with subsequent annealing in an oxygen atmosphere at high temperatures. The phase and chemical composition of the films were investigated, using X-ray phase and electron diffraction analyses and X-ray photoemission spectral and Auger emission spectral analyses. The gas sensitivity was estimated by the change in the electrical resistance of the film in the absence and in the presence of PH$_3$. The films prepared by spraying working solutions with molar ratio CuCl$_2$: SnCl$_4$ = 1:4 exhibit the highest sensitivity towards 0.1 ppm PH$_3$ ($R_{\text{air}}/R_{\text{gas}} = 15.5$) at 170°C. At this temperature, the selectivity with respect to hydrogen is at its highest (Ratcheva, Stambolova & Konstantinov 1992).
1.6 OBJECTIVE OF THE THESIS

The entire investigations of the already existing literatures reveal that the studies of chemical bath deposition of pure and doped (Mg, Cu, W & Zr) SnO\(_2\) thin films are limited compared to the other metal oxide thin films. Therefore, further investigations are needed in order to investigate the structural, optical and photocatalytic activity of SnO\(_2\) thin films which can be exploited for potential applications. A very few reports is available on the structural, optical and photocatalytic activity of pure and doped (Mg, Cu, W & Zr) SnO\(_2\) thin films prepared by chemical bath deposition method. In order to achieve the above objectives, the following works were carried out.

- To synthesise of pure and doped (Mg, Cu, Zr & W) SnO\(_2\) thin films by chemical bath deposition method.

- To analyze the crystalline nature, phase purity, average crystalline size by X-ray diffraction (XRD) technique.

- To confirm the functional group through FT-IR and FT- Raman analysis.

- To observe and to control the surface morphology and average particle size of the nanostructured thin films by using AFM.

- To analyze the optical nature of the sample such as absorption, band gap energy by UV-Vis transmittance spectroscopic technique.

- To understand the oxygen deficiency and defects in crystal, photoluminescence study will be carried out.
To evaluate the photocatalytic activities of the films were by degradation of methylene blue (MB) and rhodamine B (RHB) in an aqueous solution under ultraviolet light irradiation and to compare the efficiency of our catalyst with already existing reported values.

To disseminate the knowledge and the results of investigations through research publications, seminars, conferences and patents, etc.

1.7 STRUCTURE OF THE THESIS

The thesis is planned into eight chapters. The first chapter gives a general introduction of thin films and review of the previous work. A simple chemical bath deposition technique has been adapted to the synthesis of pure and doped (Mg, Cu, W & Zr) SnO$_2$ thin films. Structural, optical and photocatalytic properties of the thin films are studied.

The second chapter describes the characterization methods used in this present work.

The third chapter consists of materials, experimental techniques and theory of chemical bath deposition technique.

The fourth chapter deals with the structural, optical and photocatalytic activity of pure and magnesium (Mg) doped SnO$_2$ thin films.

The fifth chapter describes the results on copper (Cu) doped SnO$_2$ thin films and its structural, optical and photocatalytic properties.

The sixth chapter deals with the photocatalytic properties of tungsten (W) doped SnO$_2$ thin films by chemical bath deposition technique.
The seventh chapter describes the synthesis and systematic investigation of zirconium (Zr) doped SnO$_2$ thin films and studied their structural, optical and photocatalytic properties.

The summary and conclusion are presented in the eighth chapter.