Thin film technology is the basis of a magnificent development in Materials Science. Thin film studies have directly or indirectly influenced many areas of research based on phenomena uniquely characteristic of the thickness, geometry and structure [1]. The processing of materials into thin films allows easy integration into various types of devices. Increased efficiency with reduced size and low cost are the highlights of these tiny technical marvels. Intense and devoted research has led to a drastic improvement in understanding of thin film surfaces which in turn has resulted in an increased ability to fabricate devices with predictable, controllable and reproducible properties.

The astounding fact about thin film technologies is that the properties can be controlled and tailor made by parameters like the thickness, deposition temperature, concentration of precursor etc. The structural, electrical and optical properties of materials drastically differ when synthesized in the form of thin films. Thickness has an amazing effect in shaping up the structure and modelling the band gaps. Increase in thickness triggers a marked increase in grain size of the films [2,3]. Band gaps were found to increase with increasing film thickness [4]. The electrical conductivity has a marked dependence on the thickness factor as indicated by Fuchs Sondheimer theory [5]. Substrate temperature also plays a vital role in dictating the properties of thin film structures. Improved crystallinity and reduced resistivity have been proven with increase in deposition temperature [6]. Precursor concentration is another parameter that has a pivotal part in deciding the structural, morphological and electro-optical
properties of thin films [7]. Taking a hint from the reliable and reported findings, it has been planned to analyse the decisive role played by these deposition parameters in the properties of the research materials.

Oxide thin films with their wide range of applications as catalysts, electrodes, coatings, sensors etc. provide a rich playground for pursuing fundamental and applied research. There is a growing interest in implementing sensing devices to improve environmental safety. Thin films have proven their credibility in gas sensing. Gas sensors based on semiconducting metal oxide nanostructures are expected to exhibit better sensing properties. On view of the importance of gas sensing, it is decided to test the suitability of the study materials as sensors and to evaluate their performance parameters.

1.1 RESEARCH MATERIALS AND THEIR IMPORTANCE

Transition metals with multiple oxidation states, occupy a vital position in the periodic table on account of their unique structural, electrical and optical properties arising due to the unfilled 3d level. These oxides have drawn huge attention because of their wide use in multifunctional devices such as spintronics, magnetic recording, solid oxide fuel cells, rechargeable batteries, gas sensors etc [8].

Hausmannite (Mn$_3$O$_4$) has been widely used in electrical storage devices such as super capacitors and batteries. It has an irreplaceable part in catalysis and chemical synthesis [9-11]. Most of the rechargeable batteries for portable applications are cobalt based on account of its high energy density. The chemical stability over a wide temperature range and their high mechanical strength permits these materials to be potential candidates for field emitters. Co$_3$O$_4$ has a great potential as a catalyst in the
reduction of molecular oxygen to $O_2^-$ in alkaline solution, oxidation of hydrocarbons and carbon monoxide [12] and is being credited to have the highest capacity to exchange its lattice oxygen with atmosphere [13]. $Co_3O_4$ films exhibited excellent chemiresistive gas sensing characteristics for a host of test gases [14]. Iron (III) oxide or Hematite ($Fe_2O_3$) has a variety of applications including photocatalysis, gas sensing, magnetic recording, drug delivery, tissue repair engineering, magnetic resonance imaging, lithium-ion batteries, spin electronic devices and pigments [15-17]. These binary oxides have ignited a spark to identify and study the fundamental physics involved in these systems.

The performance of ternary spinel oxides is usually more enhanced than their corresponding binary oxides. The properties of these ternary oxides are based on their multiple oxidation states. Cobalt manganites ($CoMn_2O_4$) show excellent electrocatalytical properties [18] and are the most promising coatings for interconnect application in solid oxide fuel cells (SOFC). Manganese ferrites ($MnFe_2O_4$) show remarkable properties suitable for microwave and magnetic recording applications [19]. Recently they are also used in biomedical technologies such as cancer therapy. Spinel-type cobalt oxide based coatings have emerged as a cheaper alternative to dynamically stable electrodes in alkaline media, because they possess long-term stability under anodic conditions, good electrical conductivity and high electrocatalytic activity toward oxygen/chlorine evolution reactions [20]. In addition, these materials have huge potential in a host of solid-state applications such as gas sensors, magnetic materials, electrochromic devices, lithium-ion rechargeable batteries, fuel cells, solar absorbers, heterogeneous catalysts etc.
On account of their endless applications and curiosity evoking vital properties, transition metal oxides have been chosen as the ultimate research materials. Spray pyrolysis is an elegant chemical vapor deposition method having high degree of compositional control, direct patterning, economic viability and laboratory compatibility to its credit over other deposition methods which are hugely expensive and highly vacuum dependent. It has been proposed to spray deposit the metal oxides and characterize the prepared samples to get a first hand and clear-cut information on their properties.

1.2 PROBLEM STATEMENT

Although an enormous amount of research has been devoted to these transition metal oxides, it is surprising to find that understanding of many of the phenomena regarding binary and ternary oxides is not sufficient. This work therefore elaborates the state-of-the-art research activities that focus on these multivalent oxide systems and their physical property characterizations. It begins with the exploitation of synthesis mechanisms to form the desired nano structures suitable for device fabrication. A range of remarkable characteristics are then analysed, compiled and presented into sections covering the chosen metal oxides.

1.3 OBJECTIVES

- It is proposed to deposit three binary transition metal oxides namely Mn$_3$O$_4$, Co$_3$O$_4$ & Fe$_2$O$_3$ and three ternary oxides viz. CoMn$_2$O$_4$, MnFe$_2$O$_4$, CuCo$_2$O$_4$ by spray pyrolysis method on account of the method’s simplicity, economic viability and laboratory compatibility.
The optimized deposition conditions are to be pinpointed after trial and error attempts involving the variation of spray parameters like deposition temperature and concentration of precursor.

Several characterization techniques are to be employed on the prepared metal oxide films to bring into light their unique structural, morphological, electrical and optical properties.

Structural characterization is to be done using the reliable tool of XRD and the obtained data is compared with standard values (JCPDS) to decisively confirm the crystal structure of the prepared films. Structural parameters are to be calculated using suitable formulae.

The phase formation of the films are to be elucidated employing FTIR and the various bonds are classified with reference to the functional groups present in the prepared films.

The elemental composition and chemical nature of the films are to be revealed using Energy Dispersive Spectroscopy (EDS) and Xray Photoelectron Spectroscopy (XPS).

The shape of the grains, texture and morphology of the films is to be brought into light with the help of SEM and AFM.

The electrical parameters like activation energy, resistivity and temperature coefficient of resistance are to be found with the two probe set up.

UV-Vis-NIR spectroscopy is to be utilized to get a clear view on the optical nature of the prepared films and also to determine the band gap energy.

Photoluminescent property of the films is to be investigated by recording their PL spectra.

The properties of the transition metal oxides are to be analyzed individually and compared to pinpoint the best among them.

Ultimately based on these fundamental properties, their integration into electronic devices such as gas sensors will be tested and their sensing performance is to be evaluated.
1.4 SIGNIFICANCE & SCOPE OF THE STUDY

Sprouting smart multifunctional nanostructures and scrutinizing their material properties has given gigantic scope for sensing technologies that are aimed in alleviating environmental issues and addressing the food impairing problems. The main scope of this thesis is to develop nanostructured transition metal oxides with desired properties and explore their viability in gas sensing devices as sensing elements. This work would bring out the best performance among the metal oxides as sensors by assessing and evaluating the vital sensing parameters. Hence, it would provide an impetus and create a significant impact in the monitoring of environmental pollution and detection of food spoilage.

Moreover, investigation of the vivid material properties of the metal oxides will generate new knowledge of their electronic and atomic dynamics in condensed matter, thus leading to an improved understanding of the key role played by embedding parameters in the evolution of thin film structures.
REFERENCES


