CHAPTER I
INTRODUCTION

1.1 TRANSITION METAL OXIDE THIN FILMS

The term thin film has often been used in literatures to imply not only a layer of a solid material but also of a liquid or a gaseous phase. Further, there is neither any well-defined limit of its thickness to imply the end of the thin film stage nor one to indicate its transition to the thicker film region. All basic researchers on thin films are generally confined to a limited range of thickness between a few Å to about 5000 Å depending on the properties to be investigated. Thin film growth has been phenomenal especially due to their tremendous applications in diverse fields. The field of material science and engineering community’s ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical properties has changed the modern society. Thin film studies are one such branch that directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of the film [1].

Transition metal oxides play a very important role in many areas of chemistry, physics and materials science. The transition metal elements are able to form a large diversity of oxide compounds. Their properties range from insulating to semi-conductors, conductors or magnetic behaviors with transitions among those states. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. The diversity of such applications
originates from the more complex crystal and electronic structures compared to other class structures. The main reasons are related to their variety of oxidation states, co-ordination number, symmetry, ligand-field stabilization, density, stoichiometry and acid-base properties. The binary and ternary transition-metal oxides which form an important category of materials in fundamental physics as well as in technological applications have been attracting intense attention from the condensed matter community. These materials contain at least one transition metal ion and one or more electrochemically active/inactive ions. This class of materials has generated considerable interest due to their cheap synthesis methods, highly single crystalline surfaces and novel shapes. Their application in gas sensor technology has been explored experimentally and theoretically and in numerous cases, the developed devices show improved performance over the other traditional thin film sensors.

Among the available transition metal oxides, nickel oxide (NiO) is an attractive material due to its excellent chemical stability, as well as optical, electrical and magnetic properties. It has been used as antiferromagnetic material, electrochromic display devices and functional layer material for chemical sensors. Moreover, introduction of different valency ions (Ni$^{2+}$ and Ni$^{3+}$) makes the material non-stoichiometric by increasing the non-metallic character for p-type and metallic character for n-type. By suitably doping with different cations in required proportions modify the crystal lattice from cubic to spinel ($A^{2+}$)$[B^{3+}]_2$O$^{2-}_4$, where $A^{2+}$ and $B^{3+}$ are the divalent and trivalent cation respectively, occupying tetrahedral (A) and octahedral (B) interstitial positions of an fcc lattice formed by O$^{2-}$ ions. One such compound, spinel ferrite is one of the versatile and technologically important soft ferrite materials because of its typical ferromagnetic properties. Cobaltite and manganite spinels in turn display a vast range of fascinating electrical and magnetic
properties (colossal magnetoresistance, ferromagnetism, charge ordering and many more), which often come about due to the mixed valence states of the transition metal cations. Research described here attempts to advance the understanding of the relationship between crystal structure and cation charge state distribution among tetrahedral and octahedral sites within the spinel lattice. This is achieved using a combination of electrical and spectroscopic measurements that focus particularly on property variations with composition, with the eventual goal of being able to design spinel oxide systems with higher conductivity and optical transparency.

Thin films can be prepared by different methods such as Pulsed laser deposition [2], Magnetron sputtering [3], Molecular beam epitaxy [4], Spray pyrolysis [5] etc. Spray pyrolysis technique is used for depositing a wide variety of thin films to prepare dense and porous oxide films, ceramic coatings and powders which do not require high quality substrates or chemicals. It has been used for several decades in the glass industry and in solar cell production to deposit electrically conducting electrodes [6]. Thin films obtained by Chemical spray pyrolysis (CSP) are used in devices like solar cells, sensors, solid oxide fuel cells etc. It has evolved into an important thin film deposition technique and is classified under chemical methods of deposition. This method offers a number of advantages over other deposition processes, the main ones being scalability of the process, cost-effectiveness with regard to equipment costs and energy needs, easiness of doping, operation at moderate temperatures (100-500 °C) which opens the possibility of wide variety of substrates, control of thickness, variation of film composition along the thickness and possibility of multilayer deposition. For the present study, chemical spray pyrolysis method has been used to prepare nickel based spinel oxide thin films.
Structure and properties of the deposited films depend on spray pyrolysis parameters. The substrate surface temperature is the main parameter that determines the film morphology and properties. In many studies the deposition temperature was reported indeed as the most important spray pyrolysis parameter. The properties of deposited films can be varied and thus controlled by changing the deposition temperature. The precursor solution is the second important process variable. Solvent, type of salt, concentration of salt, and additives influence the physical and chemical properties of the precursor solution [7]. Therefore, structure and properties of a deposited film can be tailored by changing composition of precursor solution. Spray rate is yet another parameter influencing the properties of films formed. It has been reported that properties like crystallinity, surface morphology, resistivity and even thickness are affected by changes in spray rate [8]. It is generally observed that smaller spray rate favours formation of better crystalline films. Parameters like height and angle of spray head, angle or span of spray, type of scanning, pressure and nature of carrier gas, thicknesses etc. influence the properties of deposited films. Hence in the present study, a devoted step has been taken to deposit binary and ternary metal oxide thin films using the spray pyrolysis deposition method for optimizing its properties by varying the deposition temperature and precursor concentration. All other parameters such as spray rate, carrier gas pressure, distance between substrate to spray head etc. are held constant.

1.2 PROBLEM STATEMENT

Disorder in spinel or inverse spinel lattice, leads to change in cation distribution as well as change in their material properties. Study of order–disorder transition in spinel lattices is a well known problem related to mixed oxide spinels.
Moreover, incorporation of oxygen in the unit cell results in evolution of nanostructured or amorphous film. Due to incorporation of transition metal cations, the entire physical and chemical properties changes and the resultant spinel can be engaged for different applications. As NiO an electrochromic material, incorporation of Fe ions leads to magnetic properties. However, addition of Co ions makes the material as an electrode material. Hence the present problem is a related characterization study of nickel based spinel materials suitable for multifaceted applications. Thus a devoted step has been taken to prepare and characterize nickel based spinel oxides such as NiO, α-Fe₂O₃, NiFe₂O₄, NiCo₂O₄ and Ni₁₋ₓZnₓFe₂O₄ thin films for evaluating its suitability in the construction of ethanol gas sensor.

1.3 AIMS AND OBJECTIVES

The main goal of the present work is to adopt a successful method for producing thin films samples of nickel based spinel oxides and to establish the optimized deposition conditions for producing materials in the purest form as possible. For attaining the desired task, proposed steps are,

- Spray pyrolysis deposition technique has been planned for the preparation of the proposed materials, NiO, α-Fe₂O₃, NiFe₂O₄, NiCo₂O₄ and Ni₁₋ₓZnₓFe₂O₄ in thin film nanostructures with better uniformity on the substrate. Furthermore, necessary steps has been planned to study the structural properties along with the electrical, optical and magnetic properties.

- Thermal analysis (TGA/DTA) is planned to perform on the starting precursor nickel acetate to prefix the deposition temperature for the formation of well crystallized metal oxide films with optimized electro-optical properties.

- Complex oxides are difficult to deposit as thin films without loss of stoichiometry or changes in composition. So well suited characterization
techniques have to be adopted to expose the inherent properties of the materials.

- Structural characterization is vital to confirm the formation of the desired material and therefore X-ray diffraction studies have been planned to elucidate its crystal structure, unit cell parameters, density and other related parameters.

- Fourier Transform Infrared Spectroscopy has been planned to find out the oxide phase formation of the prepared thin films and to test the possibility of water adsorption on the surface of the prepared films.

- X-ray photoelectron spectroscopy (XPS) analysis is decided to perform on the prepared thin films to find out the chemical bonding state, chemical environment of the cations and their co-ordination with anions.

- Elemental composition of the prepared thin films that decides the properties of the material have to be analysed using Energy Dispersive X-ray Spectroscopy (EDAX) analysis is used.

- Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) are the viable tools decided to use to investigate the morphological nature and the size of particle/agglomerates of the prepared samples.

- It was planned to find out the optical transmittance properties and optical band gap of the synthesized thin films using UV-Vis-NIR Spectroscopy.

- D.C electrical conductivity of the prepared thin film can be measured using the standard two probe method to study the temperature dependent conductivity and the activation energy of the prepared thin films.

- Vibrating Sample Magnetometer (VSM) has been planned to perform on prepared thin films to understand the magnetic behavior.

- Optimized films may be engaged for device fabrication for a particular application. Surface modification by proper choice of additives or dopants to the base materials may be considered.

- Planned to fabricate a gas sensor using the optimized thin film samples as sensing element and to study its response behavior towards ethanol vapor.
1.4 SCOPE OF THE WORK

Proposed work will exploit the feasibility of the spray pyrolysis technique to synthesize nickel based spinel oxide nanostructures with desirable properties. Deposition parameters have to be modified for attaining good quality thin films. Quality of the films can be confirmed from the decided studies performed using sophisticated analytical tools. After deposition, that can be applied to study the effect on material properties as well as to identification of good quality films that can be engaged for their potential use in developing miniaturized devices. The physical flexibility of the chosen spinel compounds provides the possibilities for a wide range of physical behavior that offer great opportunities for practical application. The work will conclude with a potential outlook of some scientific and technological challenges that remain for further exploration in this field.

1.5 IMPACT

Study of spinel binary oxides with in-depth understanding in embedded parameters of the system leads to establish the conditions for producing the purest possible material. Also, the study offers enormous opportunities in interdisciplinary areas and gives a new dimension to the fabrication of new miniaturized devices.
REFERENCES


