CHAPTER I
INTRODUCTION

Thin film technology is the basic of astounding development in solid state electronics. The unique properties of two-dimensional materials have been responsible for the immense interest in the development of new devices for diverse applications. Hence studies on thin films have directly or indirectly advanced many new interdisciplinary areas of research due to its unique character that depends on thickness, geometry and structure [1]. Advances in thin film deposition techniques in the 20th century have enabled a wide range of technological breakthroughs in the diverse fields of electronics, optics, space science, aircraft, defence and other industries. These investigations have led a numerous inventions in the forms of active devices and passive components, piezo-electric devices, micro-miniaturization of power supply, rectification and amplification, sensor elements, storage of solar energy and its conversion to other form, magnetic memories, superconduction films, interference filters, reflecting and antireflection coatings and many others [2].

Among the available materials, Transparent Conducting Oxides (TCOs) are degenerate wide band gap semiconductors with conductivities comparable to metals but are transparent over the visible or IR regions. CdO films were the first reported transparent conducting oxide [3]. Ingram et al. classify TCO structurally into four main families [4]. The first family has cations tetrahedrally coordinated by oxygen and is n-type in character. ZnO is the only known oxide to possess this coordination exclusively. The second family has cations in octahedral 16 coordination and is also n-type in character. This is the largest family of TCOs, including CdO, In$_2$O$_3$, SnO$_2$
and most of the best n-type complex oxide materials. The third family of TCOs has cations in linear coordination with oxygen and is p-type in character. This family includes CuAlO$_2$, related Cu- and Ag-based delafossites. Finally, the cage-structured composite oxide, 12CaO·7Al$_2$O$_3$, is listed as the first member of a potential new family of TCOs; it is n-type in character.

Delafossites is a subset of the much larger group of AMO$_2$ compounds with transparency and conductivity [5-19]. Delafossite structure is one composed of an alternating stack of O-A-O “dumbbells” and [MO$_6$] edge sharing octahedral and is divided between two polytypes, the 3R rhombohedral crystal structure and the similar 2H hexagonal structure. The point group symmetry for the two polytypes is R̅3m and P6$_3$/mmc respectively. The basic construction of O-A-O dumbbells and [MO$_6$] polyhedral are the equivalent but the 3R delafossite forms in a ABCABC… stacking sequence, whereas the 2H delafossite has its polyhedral layers rotated 180º to each other in a ABABAB… sequence. Both polytypes are illustrated in Fig. 1.1.

![Fig. 1.1 Crystal structure of delafossite: (a) 3R and (b) 2H polytypes](image)
During the last few decades, transition metal oxide thin films have been attracted and used in a variety of applications such as gas sensors, solar cells, heat reflectors, transparent electrodes, flat panel displays, solar energy capture and other opto-electronic devices. However, among all metal oxides, a few materials dominate the current TCO industry. Being a TCO, Copper Oxide has gained increasing attention because of its low price, good gas sensing properties, fabrication of thin film solar cells [20-23] and also used as a coating agent on the sliding face of precision devices, turbines, vacuum breakers and aero-spatial driving materials [24]. From literature survey, it is observed that the properties of CuO material can be tuned to suitable application depending on the type of devices, geometry and expected performance. Also its delafossite structured (CuAlO$_2$, CuFeO$_2$, CuCrO$_2$, CuMnO$_2$) thin films have been chosen as the current research materials due to their vital properties and infinite applications.

Since preparation is instrumental in deciding the properties of thin films, a wide range of deposition techniques has been adopted to synthesize CuO and its delafossite structured (CuAlO$_2$, CuFeO$_2$, CuCrO$_2$, CuMnO$_2$) thin films. Some of the reported preparative methods are sol–gel technique, one-step solid-state reaction, an electrochemical method, pulsed laser deposition, thermal oxidation, chemical bath deposition, microwave, electro-deposition and sputtering [25-31]. All these preparation techniques offer distinct advantages depending on the kind of application. Most of the techniques need to work at low-pressure atmosphere and need corresponding vacuum system, which is expensive and complex. Therefore, it is a critical issue to find a suitable method, which can get the low-cost deposition of films with high quality and on a large scale.
In many applications, large area coating is essential and chemical spray pyrolysis is a technique which could be used for the production of large-area thin film deposition without using a high vacuum system. Also in this system, the complete decomposition of sprayed solution taken place in the reaction chamber and the material is deposited on the substrate surface which is kept at the desired temperature. In view of this, the present problem has been planned to carry out the deposition of CuO and its delafossite structured thin films using spray pyrolysis technique and to mine the properties of the study materials for testing its suitability as sensing element in a gas sensor.

1.1 PROBLEM STATEMENT

Thin film technology is significant due to its miniaturization and the curiosity to improve the characteristics for diverse applications. Transparent conducting oxides (TCOs) play a pivotal role in combining high optical transparency coupled with electrical conductivity which forms the basis of many important technologies including flat panel displays, solar energy capture and other opto-electronic devices. Moreover, the variation in the chemical and physical properties of TCOs is the origin of the diverse technological applications.

Although researches on Copper Oxide and its delafossite structured (CuAlO₂, CuFeO₂, CuCrO₂, CuMnO₂) thin films have been studied, their properties are still not well understood due to the diverse nature of the samples obtained from different deposition techniques and parameters. So the current research focuses on the linkage between synthesis and processing conditions and the property variations of the chosen materials. Hence the stated problem focuses on synthesizing Copper Oxide and its
delafossite structured (CuAlO$_2$, CuFeO$_2$, CuCrO$_2$, CuMnO$_2$) thin film nano structured oxides using chemical spray pyrolysis technique. Processed thin films structures are engaged for property analysis to understand the suitability as sensing element in ethanol gas sensors.

1.2 OBJECTIVES

The main objective of the proposed research problem is to prepare high quality Copper Oxide and copper based delafossite structured metal oxide nanostructures exhibiting novel and unique properties that will shed light on key unresolved questions concerning the properties of materials and their variations with preparative conditions. Optimization of preparative conditions on the basis of obtaining quality films with desired properties is the aim of the present problem. Engaging quality films with suitable character towards fabricating a device is the key plan of the stated problem. For attaining the desired objectives, following approaches have been planned.

- Proposed research problem aims to synthesize CuO and copper based delafossite structured transparent conducting oxide thin films (CuAlO$_2$, CuFeO$_2$, CuCrO$_2$, CuMnO$_2$) using the chemical spray pyrolysis technique by varying substrate temperatures and precursor concentrations.

- After preparation, the study focuses the property extraction of the nanostructures using advanced and sophisticated instrumentation. Based on the obtained parameters, preparative condition optimization is planned as next step. For property extraction and analysis, following tools are engaged.

  (i) Prior to deposition, thermal analyses on the starting precursor salt have been planned using TGA/DTA to fix the substrate temperature range for the formation of metal oxide films.
(ii) The thickness of all the prepared samples has to be measured by using Stylus Profiler.

(iii) X-ray diffraction (XRD) and FT-IR spectroscopy have to be employed to study structural information and to estimate the bonds that confirm the formation of proposed metal oxides.

(iv) X-ray photoelectron spectroscopy (XPS) and Energy Dispersive Absorption of X-ray analysis (EDAX) have to be performed to identify qualitatively and quantitatively the chemical composition and the chemical environment of various ions in the processed thin films.

(v) Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) have to be engaged to visualize the surface nature including surface roughness and level of aggregation of the grains.

(vi) The electrical study has to be done to find the type of conduction in films and the mechanism behind conduction.

(vii) UV-Visible spectroscopy has to be employed to study the absorption tendency, transmission level and band gap energy values and their variations.

(viii) Defect structure estimation has to be done using Photoluminescence Spectroscopy by noting the emission lines for a specific excitation.

(ix) Finally, on the basis of the exhibiting properties of the study materials, its suitability to serve as sensing element in ethanol gas sensor has been planned.

1.3 SIGNIFICANCE AND SCOPE OF THE STUDY

With the aid of wet chemical processes, inorganic compounds can be created as 2D – nanostructures with a high degree of control over its crystalline character and surface morphology simultaneously. By developing a comprehensive ability to pattern inorganic nanostructures for various thicknesses, the study signifies the possible method to design complex materials in which several microscopic processes are
independently and simultaneously optimized. Enabling the deterministic assembly of high surface-area metal oxide thin films, the study helps to process nanostructured assemblies with enhanced electronic properties suitable for advanced active devices.

The scope of the present study will generate new fundamental knowledge regarding the delafossite metal oxides and the way to deposit it and to characterize it for a specific task. As materials science is interdisciplinary, present study helps to construct thin structures with desired qualities for engaging them in the field of chemistry, engineering and other related areas for the fabrication of transparent nano active devices.
REFERENCES


