1 PREFACE

1.1 Introduction

The last few decades witnessed a remarkable achievement in the area of thin film processes, primarily as a result of the ever-increasing demand for thin films of insulating, dielectric and conducting materials for a variety of device applications. In addition to device applications, thin film studies have also 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 films.

The techniques for the production of the films have been intensively studied for many years, especially in the last few decades. Advancements made in the area of ultra high vacuum techniques have triggered significant developments in thin film deposition techniques ranging from the conventional thermal evaporation to the more sophisticated molecular beam epitaxy. Apart from these, considerations of simplicity, economics, input energy and large area coatings have inspired researchers to grow thin films using another mode of film deposition, namely, the chemical deposition technique.

In recent years, research activities on transparent conducting oxide (TCO) films have increased tremendously. These films are widely used today in most of the optoelectronic and solid state devices such as display electrodes in flat panel displays [1], photovoltaic cells [2], gas sensors [3], heat-reflecting filters [4], production of heating layers which protect vehicle wind-screens from freezing and misting over [5], antistatic surface layers on temperature control coatings in orbiting satellites [6], antireflection coatings [7], high sensitivity photodetectors [8], vidicons [9], electro-optic shutters in high energy solid state laser systems [10] and protective coatings to glass containers [11]. Due to these facts, increasing demands have stimulated, in recent years, the production of transparent conductors in thin film form. Numerous materials have been reported in the literature in which the simultaneous occurrence of high
transparency in the visible and near infrared region of the spectrum and a significant electrical conductivity are possible.

There are two types of materials which possess these special properties. They are metal and metal oxide films. The metals that have been used as transparent conductors are Au, Pt, Rh, Ag, Cu, Fe, Ni and many of these materials coated onto the top of various materials which affect the nucleation and growth of the metal films [12]. For example, gold films directly deposited on glass at normal temperatures do not develop a connected structure which is conducting until a thickness of about 40 Å is reached, but when deposited on a sputtered bismuth oxide base-coating, gold films become conducting when only 15-20 Å thick. The apparent function of the dielectric layer is to reduce the mobility of the gold atoms on the substrate surface, thereby preventing the formation of an agglomerated structure [13]. The metallic films have difficulty in simultaneously being both highly transparent and highly conducting, since, the nucleation and growth mechanism of metal films leads initially to the formation of island structures which are discontinuous and so of high sheet resistance. If deposited sufficiently thick to form a continuous coating, the film is more absorbing and transparency is compromised by conductivity.

The other kinds are a few metallic oxides. They are classified as tin oxide (SnO₂), indium oxide (In₂O₃), zinc oxide (ZnO), cadmium oxide (CdO) and their compounds.

The three important properties of the films are

(1) a wide bandgap, responsible for their excellent transparency in the visible and near infrared regions and high reflectivity in the infrared region of the electromagnetic spectrum

(2) non-stoichiometric nature, mostly in the form of defects such as metallic interstitials and oxygen vacancies, giving rise to a significant electrical conductivity and

(3) high carrier mobility and low effective mass

If these oxides are fully stoichiometric, then they act as perfect insulators. For these materials to be highly conducting, the carrier density must be 10²³ m⁻³ or more. This can be achieved by creating defects
as mentioned above. For instance, if a doubly charged oxygen ion is removed from the lattice site of the crystal, then two negatively charged electrons have to be formed to conserve the charge neutrality of the crystal. The neutral oxygen may thus be considered as a doubly charged oxygen vacancy with two trapped electrons. The neutral vacancy may thus act as a donor leading to the release of these trapped electrons for the electrical conductivity. Carrier density can also be effectively increased by keeping the metallic atoms in the interstitial sites. For instance, in a perfect tin oxide lattice, a tin atom may be located in an interstitial site with its valence electrons not particularly bound to anything. Apart from these, the other properties that are considered important include the environmental stability, the chemical nature, the structure and morphology of the film surface.

Mobility is also a key to successful conduction in transparent conductors. Factors that contribute to mobility include the connectivity or continuity of the film, impurities including the dopant atoms themselves that disrupt the band structure, crystallinity and grain structure and finally the effective electron mass.

As a direct consequence of electromagnetic theory, perfect electrical conductivity and complete transparency in any material represent a contradiction, because the incoming electromagnetic wave is dissipated by heating the charge carriers. Besides this, there are numerous other sources of light loss which depend upon the film material, its structure and surface morphology. The practical consequence of this is that, there is a trade off between the electrical conductivity and the transmittance [12].

Extensive research has already been carried out on SnO$_2$, In$_2$O$_3$ and ZnO thin films. Cadmium oxide (CdO) is also a promising representative of this group. However, it shows an absorption edge in the visible region of the spectrum and appears yellowish in colour and this problem can be sorted out by adding appropriate dopants like tin and indium. The advantages of cadmium oxide thin films are their best electrical properties along with the indium oxide thin films. Also, cadmium is much cheaper than indium and hence it is cost-effective to produce cadmium oxide films than indium oxide films.
A factor of great concern is that cadmium is being avoided in most applications because of the environmental hazards involved in the production of CdO and the use of this material. Therefore, care must be taken during the preparation of CdO films. Though cadmium is harmful, literature survey points out that films of CdO have been prepared by a few researchers. On line with these reports, the present investigation is an attempt to produce and characterise these films by DC reactive magnetron sputtering and spray pyrolysis.

1.2 Survey of Literature

Least work has been done on the physical properties of cadmium oxide thin films. It is an n-type wide bandgap (≈ 2.4 eV) semiconductor. Its structure is of the cubic type (NaCl type) with a lattice parameter of 4.695 Å and density 8 g/cm³ [14]. It shows n-type conductivity of the order of $10^5$ to $10^6$ Ω⁻¹ m⁻¹, which results from the presence of cadmium interstitials and oxygen vacancies acting as donors. These films are useful for a wide range of applications such as solar cells [15], phototransistors [16], photodiodes [17], photocells [18,19], transparent electrodes [20] and gas sensors [21].

Many methods have been used to fabricate these oxide materials. Various process parameters are involved in the deposition techniques which in turn directly affect the film properties. Helwig [22] has reported the electrical and optical investigations of CdO films prepared by reactive sputtering. The report contains a detailed account of the electrical conductivity of cadmium oxide films depending on the sputtering conditions. He showed that the conducting properties were due to the inclusion of excess cadmium atoms in the lattice and related the partial pressure of oxygen in the sputtering gas to the conductivity of the deposit, which after heat treatment in air tended to reach a constant and high value of conductivity irrespective of the initial value. Holland and Siddall [13] have reported the properties of these films formed by reactive sputtering. They have prepared CdO films using gas mixtures of argon and oxygen and studied the resistance stability of these films. Lakshmanan [23] has studied undoped, indium and copper doped cadmium oxide thin films prepared by reactive
sputtering. The oxygen vacancy concentration in these films was changed by varying the oxygen pressure in the sputtering chamber. Lewin et al have prepared various kinds of transparent conducting oxides of metals such as indium, cadmium, tin and zinc and alloy oxides of a combination of these materials by reactive magnetron sputtering from elemental targets. These researchers observed that cadmium oxide along with indium oxide is found to be most conducting and stable with resistivities of $4 \times 10^{-6} \Omega m$ being obtainable with good visual transparency [24].

Tanaka et al [25] have made investigations on these films prepared by reactive sputtering method with various sputtering voltages. Their observations on lattice parameters lead to the conclusion that CdO films with higher carrier concentrations contain some amount of interstitial excess cadmium atoms. Recently, Chu and Chu [26] have reported characterization on the spray pyrolytically coated and sputter deposited CdO thin films. These authors have reported electrical resistivities of $(2-5) \times 10^{-5} \Omega m$, carrier density of approximately $10^{20} m^{-3}$, an optical transmittance higher than 70% in the wavelength range 600-900 nm and an optical bandgap of 2.4 to 2.42 eV for films of typical thickness 500 nm.

Sravani et al [27] have reported these properties on the activated reactive evaporated CdO thin films and the film resistivity and transmittance were found to be influenced by the glow power of the discharge. Phatak and Lal [28,29] have also made extensive investigations on the various properties of these films formed by activated reactive evaporation technique. Ferrer [30] has reported the characterization of CdO thin films obtained from thermal oxidation of metallic cadmium by electrolyte electroreflectance (EER) and photoelectrochemical measurements and obtained high values of direct bandgap between 2.5 and 2.7 eV by these two different methods.

Ocampo [31] et al have reported the preparation and characterization of large area CdO thin films by a low cost technique, viz. the chemical bath deposition using a solution containing a mixture of cadmium acetate, ammonia and distilled water. The resulting films were found to have high transmittance and a bandgap of about 2.2 eV. Varkey and Fort [32] have reported the preparation of thin films of cadmium oxide on glass substrates from a chemical bath containing cadmium ammine complex ions. The films of
typical thicknesses 200 to 600 nm, were found to have a transmittance of over 85 % in the spectral range 530-900 nm and an optical bandgap of 2.3 eV. The films have room temperature resistivity of $(2-5) \times 10^{-4}$ $\Omega$ m.

1.3 Scope of the Present Work

A thorough analysis of the literature reveals that CdO films require further investigation to make them viable for commercial applications mainly in optoelectronic devices where optimum transmittance and conductivity are essential. Bearing this in mind, the present work is devoted to the preparation of good quality CdO films. It is well known that the properties of the films are extremely sensitive to the mode of preparation and the deposition conditions. Hence, it is essential to determine the structural, composition, electrical, optical and laser damage properties, all simultaneously, in order to correlate them and to get a better insight into the nature of cadmium oxide thin films.

The object of the present work involves the preparation of CdO thin films produced by spray pyrolysis and DC reactive magnetron sputtering and the characterisation of the prepared thin films. Though spray pyrolysis and DC reactive magnetron sputtering are the standard techniques employed to prepare thin films, these two techniques have been developed for the first time in this laboratory. Quite a number of days have been spent in standardising these two methods for the film preparation. In fact, DC reactive magnetron sputtering technique is adopted for the first time to prepare cadmium oxide thin films. Also, in the characterisation of the films, much efforts have been taken to analyse in detail the structure of the films which is not available in the literature. Auger electron spectroscopy and Rutherford backscattering spectrometry have been employed to analyse thoroughly the composition of the prepared CdO samples. Laser damage threshold studies of the CdO films have been performed for the first time.

Cadmium nitrate has been used as the starting material for the CdO film deposited by spray pyrolysis. In the case of DC reactive magnetron sputtering, a mixture of $N_2 + O_2$ is preferred to sputter the cadmium target, since the conductivity of CdO films sputtered in $N_2 + O_2$ mixture
is found to be higher than the films sputtered in Ar + O₂ mixture [33].

The present thesis consists of eight chapters.

The first chapter is of introductory nature. The importance of TCO's and their usefulness in a variety of commercial applications are underlined. A brief survey of literature is also given followed by the scope of the present work.

A description of the various experimental techniques adopted in the present investigation is given in second chapter. Selection of the substrates, the procedure used to clean them, the coating techniques such as spray pyrolysis, DC reactive magnetron sputtering and vacuum evaporation and the various methods for the film thickness determination have been discussed.

The third chapter describes the X-ray diffraction technique adopted to get an idea of the structure of these films. The procedures to calculate the different structural parameters such as lattice parameter, crystallite size, dislocation density, strain and stacking fault probability are given and the results are discussed in this chapter.

The composition analysis of cadmium oxide films by Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES) techniques are discussed in brief in chapter four.

In the fifth chapter an account of optical properties of the prepared cadmium oxide thin films is given. The various optical constants and the electrical band gap energy have been determined from the optical measurements.

The sixth chapter deals with the electrical properties of cadmium oxide thin films. Hall effect and thermoelectric power measurements have been used in the present work. The effect of deposition conditions for both the sprayed and sputtered CdO thin films has been investigated. The type of conduction mechanism dominating the mobility of the films has also been analysed.

The laser induced damage studies on cadmium oxide thin films have been reported in the seventh chapter. The damage threshold density as a function of substrate temperature for sprayed as well as sputtered CdO films has been
evaluated and the results are discussed in terms of other parameters of the films such as refractive index, void concentration etc.

The last chapter presents a summary of important conclusions drawn from the various studies carried out and the scope of future work on CdO thin films.

A part of the results presented in the thesis has been published in the following conferences and journals.

1.4 List of National / International Conference Papers

(1) Structural, optical and electrical properties of cadmium oxide films deposited by spray pyrolysis
K. Gurumurugan, D. Mangalaraj, S. K. Narayandass and C. Balasubramanian
Seventh International Workshop on Physics of Semiconductor Devices, National Physical Laboratory, New Delhi, India (1994) 520

(2) Electrical properties of CdO films deposited by spray pyrolysis
K. Gurumurugan, D. Mangalaraj, S. K. Narayandass and C. Balasubramanian

(3) Characterization of magnetron sputtered cadmium oxide thin films
K. Gurumurugan, G. Kumar Sathian, S. Sakthivel, D. Mangalaraj and S. K. Narayandass
National Conference on Thin Film Processing and Applications, Sri Venkateswara University, Tirupaty, India (1995)

(4) Magnetron sputtered transparent conducting CdO thin films
K. Gurumurugan, D. Mangalaraj and S. K. Narayandass
Accepted for presentation at 37th Electronic Materials Conference University of Virginia, Virginia, USA, June 21-23, (1995)

1.5 List of International Publications

(1) Structural, optical and electrical properties of cadmium oxide films deposited by spray pyrolysis
K. Gurumurugan, D. Mangalaraj, S. K. Narayandass and C. Balasubramanian
Physica Status Solidi (a), 143 (1994) 85
(2) Characterization of transparent conducting CdO films deposited by spray pyrolysis
Semiconductor Science and Technology, 9 (1994) 1827

(3) Correlations between the optical and electrical properties of CdO thin films deposited by spray pyrolysis
K. Gurumurugan, D. Mangalaraj and Sa. K. Narayandass
Thin Solid Films (Letters Section), 251 (1994) 7

(4) Structural characterization of Cadmium oxide thin films deposited by spray pyrolysis
K. Gurumurugan, D. Mangalaraj and Sa. K. Narayandass

(5) An approach to determine the refractive index of Cadmium oxide thin films
K. Gurumurugan, D. Mangalaraj and Sa. K. Narayandass

(6) Influence of substrate temperature on the physical properties of sprayed CdO thin films
K. Gurumurugan, D. Mangalaraj, Sa. K. Narayandass, K. N. Krishna, B. Sundaravel and Arjun Gopalakrishna

(7) DC reactive magnetron sputtered CdO thin films
K. Gurumurugan, D. Mangalaraj, Sa. K. Narayandass and Y. Nakanishi

(8) Laser-induced damage studies on cadmium oxide thin films
K. Gurumurugan, D. Mangalaraj and Sa. K. Narayandass

(9) Magnetron sputtered transparent conducting CdO thin films
K. Gurumurugan, D. Mangalaraj and Sa. K. Narayandass
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