CHAPTER (1)
INTRODUCTION

1.1. TCCs: CURRENT STATUS AND CHALLENGES

One of the most important fields of current interest in materials science is the fundamental aspects and applications of transparent conducting thin films. The characteristic properties of such coatings are low electrical resistivity and high transparency in the visible region. Though early work on these films was performed out of purely scientific interest, substantial technological advances in such films were only made after 1940. This is mainly due to the potential applications of transparent conducting oxides (TCOs) both in industry and research. The first report of transparent conducting thin films of cadmium oxide (CdO) was given by Badeker [1]. Transparent and conductive layers of some metallic oxides, such as CdO, SnO$_2$, In$_2$O$_3$, ZnO, and cadmium stannate have been known for a long time [2-3]. Thin films (~100-200Å) of metals such as Au, Ag, Cu, Fe, etc. have also been found to have similar properties, but these films are not very stable and their properties degrade with time [4]. However, metal oxide coatings are preferred in various applications because of their several advantages over the noble metal based coatings. These n-type semiconductors show high visible transmittance and high IR reflectance together with low resistivity. This is due to wide band gap characteristics, moderately high carrier concentration and high mobility. Besides this, the TCO coatings are economically viable and do not show any chemical or mechanical aging, which enables their use on glass or polymer substrate [5] depending on their specific applications.

Such spectrally selective films have wide applications in window and thermal insulation in lamps [6-7]. TCO films have proven their utility as transparent electrical heaters for windscreens in the aircraft industry. Recently, these transparent conducting coatings (TCCs) have been extensively explored in a variety of other applications such as thin film solar cells (TFSCs), gas sensors, heat reflectors, protective coatings, optoelectronic devices etc. Particularly, in photovoltaic and photo thermal devices, TCCs play an important role in enhancing energy conversion efficiency. Thin Film Solar Cells (TFSCs) with an integral transparent conducting layer offer the possibility of fabricating low cost solar cells with performance characteristics suitable for large scale terrestrial applications. The use of TCC in TFSC permits the direct transmission
of solar radiation to the active region with little or no attenuation. In addition, the TCCs can serve simultaneously as a low resistance ohmic contact to the junction and antireflective coating for the active region. Thin film solar cells utilizing TCCs are fabricated using many materials such as SnO$_2$/Si, In$_2$O$_3$/Si, ITO/Si [8], ZnO/Si, ZnO/a-Si:H, ZnO/µc-Si:H [9-14] and ZnO/CdS/Cu$_2$S and ZnO/CulnSe$_2$ [15-17]. Heterojunction based TFSCs of these type are potential candidates for photovoltaic applications. The future of thin film solar cell (TFSC) technology gives an optimistic impression. However, extensive research work is required to be done to establish its utility for device applications. The cost-effective large-scale production of TCCs with functional adaptability and improved optoelectronic properties are key challenges in the field of production, research and development in photovoltaics (PV).

The basic properties of these films that are most important for practical applications are structural morphology, electrical resistivity and optical transmission. Since the optoelectronic properties depend strongly on microstructure, stoichiometry and the nature of impurities present, the growth technique plays an important role. With the increasing sophistication of device based on TCCs, there is a need for improving quality and understanding of the basic properties of these films. The mechanisms of doping and conduction are still inadequately understood. Compositions are still quoted without adequate detailed analysis, especially the oxygen concentration. Novel TCC based devices, with enhanced smart functionality and characteristics performance are therefore under investigation by many researchers. In addition, new developments in inexpensive techniques for the growth of these films on large areas appear to hold considerable promise in the near future.

1.2: RATIONALE FOR THE PRESENT WORK

Zinc Oxide (ZnO) is one of the most important wide bandgap semiconductor materials ($E_g \approx 3.3$eV) with hexagonal wurtzite structure. It shows excellent combination of structural, electrical and optical properties. In addition ZnO is more ideal Transparent Conducting Oxide (TCO), due to its high chemical and mechanical stability in hydrogen plasma, high optical transparency in the visible and near-infrared region with non toxicity and low cost of synthesis. Thus it is cheap transparent conducting electrode and antireflection coating for low cost thin film solar cell (TFSC) applications [18]. However, the development of process technologies
providing an optimum film quality on large areas at high growth rates are an essential prerequisite to meet the low cost targets in TFSC production.

Recently research on ZnO has experienced renaissance due to its identical and closely matched crystal lattice structure with GaN. ZnO therefore offers potential as a substrate material on which high quality GaN films may be grown [19-22]. ZnO has the large exciton binding energy (60 meV) as compared with GaN (25 meV) [23, 24]. With the advent of modern thin film deposition techniques for oxide films, direct integration of ZnO onto a variety of substrates is quite feasible. This requires clear understanding of the material employed in the device and growth techniques with excellent reproducibility. The growth techniques offering a better control over structural, optoelectronic and piezoelectric properties led to a variety of applications as integrated optical and gas sensors, ultraviolet laser, light-emitting diodes, photodetectors [25-26], surface acoustic wave (SAW) devices [27], and thin film actuators [28]. Influence of various dopants in ZnO revealed potential applications in the area of UV light detection [29], spin functional devices [30], optical waveguides and acousto-optic media [31,32]. Significant improvements in the processing technologies and a better understanding of the semiconducting properties of ZnO have now intensified the efforts for possibly achieving p-type doping in ZnO to develop novel device structures useful for transparent opto-electronic devices. Recently ZnO thin films have also been studied as an active channel material in thin film transistors [33, 34].

The recent reports on nanotubes, nanobelts, nanorods and nanowires [35-41] of ZnO have drawn considerable attention because of their distinct and superior properties like small sizes and large surface to volume ratio. These unique nanostructures demonstrate that ZnO probably has the richest family of nanostructures amongst all materials, both in structures and in properties. Extensive research and development efforts on ZnO thin film growth have been underway and device quality films have been deposited successfully by a variety of deposition techniques. These include Physical Vapour Deposition [40], Thermal Oxidation [41-45], Chemical Spray Pyrolysis (CSP) [46], Screen Printing [46], Sol Gel Synthesis [47], Ion Beam Assisted Reactive Deposition [48], Sputtering [49-51], Modified Electron Cyclotron Resonance (ECR) [52], Chemical Vapor Deposition (CVD) [53], Pulsed Laser Deposition (PLD) [54], and Molecular Beam Epitaxy (MBE) [55]. Amongst all these techniques Sputtering, MOCVD, MBE, PLD, and CSP are the foremost that have

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been able to produce device quality films. The CSP technique has acquired considerable attention because of its simple approach, inexpensive apparatus, ease of commercialization and capability to have large area deposition. Besides the above mentioned advantages CSP technique has its own merits such as

1. Structural and optoelectronic properties of deposited materials can be tailored by proper optimization of process parameters,
2. CSP permits an easy way for doping with different dopant to the desired level,
3. Films are reproducible, uniform and adherent to the substrate.

Many reviews, in this field, which have been published up to now, have concerned themselves with deposition techniques, properties and applications. There have also been a number of conferences over the years on understanding and facilitating further substantial advances in this scientifically exciting and technologically profitable area.

1.3: AIM AND OUTLINE OF THE WORK

The present study has been done with intention of investigating the feasibility of the CSP technique to synthesize good quality undoped and Al, Cu and Cd doped ZnO films for TCC applications. Amongst various TCOs, most popular are SnO$_2$:F and In$_2$O$_3$:Sn. These have been extensively used for variety of applications and hence investigated in detailed. On the other hand although doped ZnO films show almost similar properties, with far better variety of applications have remained relatively unexplored. It should be noted that ZnO based film offers a number of advantages over their counterpart viz. CdO, SnO$_2$, In$_2$O$_3$, and cadmium stannate, as they

1. Consist of nontoxic, cheap and abundant elements,
2. Are easily produced by Spray Pyrolysis Technique, which is preferred for large-scale coatings,
3. Allow tailoring of the ultraviolet absorption because the fundamental band gap of ZnO lies just at the end of the luminous spectrum,

If highly transparent and conductive ZnO based films could be made with inexpensive thin film deposition technique, the films could be used as less expensive transparent electrodes for TFSCs. Our investigation started with optimization of process parameters such as substrate temperature, solution flow rate, air flow rate etc. for undoped ZnO thin films.
All the transparent conducting films have n-type conductivity. The high conductivity of these films is mainly a result of stoichiometric deviation. The non-stoichiometric films have excellent electrical and optical properties, but, optoelectrical properties of undoped non-stoichiometric films are not stable at high temperatures. The conduction electrons in these films are supplied from donor sites associated with oxygen vacancies or excess metal ions. These donor sites can easily be created by chemical reduction. For both flat panel display and photovoltaic applications nonstoichiometric films are inferior. Therefore, non-stoichiometric film need to be doped with suitable impurity atoms at either cation or anion sites, thereby doped nonstoichiometric films can be made to have very stable optical, electrical properties. Doped films however are found more stable and their optoelectronic properties do not degrade over a period of time as in case of undoped ZnO films.

In order to improve the stability of ZnO films as a good TCC, we have intentionally doped ZnO films using different metal ions viz. Al, Cu and Cd. The effect of substrate temperature and dopant concentration has been investigated in detail on structural and optoelectronic properties of doped ZnO films. This has been done to get the best opto-electronic properties of Al, Cu and Cd doped ZnO thin films. The objective of the present work is to deposit good quality Aluminum, Copper, and Cadmium doped ZnO films using CSP technique to be used as TCC in TFSC technology. The crystal structure, orientation, surface morphology, optical and electrical properties of the films synthesized using CSP technique have been investigated by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Ultraviolet-Visible-Near IR (UV-VIS-NIR) spectroscopy and Hall effect (Van der Pauw geometry) measurement techniques. The optoelectronic properties are correlated with their structural properties and process parameters.
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