CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The science and technology of thin films have made revolutionary changes in microelectronic industries and even today they continue to be recognized globally as frontier areas of research. Thin film technology gains paramount importance since it unravels the complex nature of electronic systems. The obvious reason for preparing materials in the thin film form and studying their properties is that, two film surfaces are very close to each other and they can have a decisive influence on the internal physical properties. These properties differ in a profound way from those of bulk material. The technical interest into the study of the properties of thin films has resulted in the invention of important devices such as solar cells, active and passive microminiaturized components, magnetic memory devices, reflection and anti reflection coatings etc., Within the last few years, the improvement in the experimental techniques have begun to exercise a conclusive influence on the progress of thin film studies.

The Sputtering, Electron Beam Evaporation, Hot Wall Deposition, Molecular Beam Epitaxy etc., techniques are used for the preparation of good quality thin films. The above physical vapour deposition (PVD) methods are comparatively expensive as compared to chemical vapour deposition methods (CVD) due to some shortcomings such as small area deposition, requirement of sophisticated instruments, high working cost, extreme cleaning of system after each deposition. On the other hand, the chemical bath deposition methods are low cost processes and the deposited films are found to be of comparable quality to those obtained by more sophisticated and expensive deposition process. CBD methods are capable of producing metal oxide films at relatively low temperatures. For deposition of the ZnO thin films, among the chemical deposition methods, most of the researchers have fascination towards the chemical bath deposition (CBD) method [1–3]. The CBD method uses the principle of solubility product and ionic product, where the film formation on substrate takes place when ionic product exceeds solubility product by heterogeneous nucleation onto the substrate. However, simultaneously this results in unnecessary formation of precipitate in the solution by homogeneous nucleation and loss of material.
However, it is necessary to modify this method in order to avoid such unnecessary bulk precipitation. One such alternative, which avoids, unnecessary precipitate formation in the solution, is successive ionic layer adsorption and reaction (SILAR) method. In this modification, thin films are obtained by immersing substrate into separately placed cationic and anionic precursors [4]. Thus, precipitate formation in the solution, i.e. wastage of material, is avoided in SILAR method. The optimization of durations of immersion of substrate into the cationic and anionic baths is critical for ionic layer formation.

Generally, acquiring good quality films are not possible by CBD technique, because thin film formation depends on chemicals, their concentration, temperature of hot bath, pH value of the solution, dipping time and withdrawing speed of the substrate. We have has designed and fabricated an instrumental set up to overcome the above difficulties. The designed instrumental setup is used to control precisely the up/down movement of substrates, withdrawing speed, position of the substrate in the chemical bath, dipping time, temperature of chemical bath and also to use more than one chemical bath.

The zinc oxide (ZnO) thin films have unique combination of interesting properties such as non-toxicity, good electrical properties, high luminous transmittance, excellent substrate adherence, hardness, optical and piezoelectric behaviour, stability in a hydrogen plasma atmosphere and its low price [5,6]. It has proved its competence in variety of practical applications; light emitting diodes [7], photo detectors [8], piezoelectric cantilever [9], gas sensors [10], and buffer layer in CIGS solar cells [11], and dye sensitized solar cells [12] and recently ZnO layer has been used to improve the performance of TiO$_2$ in the [13]. In addition, the ZnO has relatively high physical and chemical stability, and hence it has many high temperature applications, such as buffer for III–V nitrides [14]. Therefore, it is not surprising that it has been under intensive investigation and many methods have been employed for preparation of such a significant material in thin film form.

The designed instrumental setup was used to prepare the ZnO thin film by employing SILAR technique. The thin films were formed by dipping the substrate in two different chemical baths for fixed time. The preparation of films was done by changing
the absorption rate and reaction rate. The prepared films were characterized and the characterized results were compared with the standard results. The thermal behavior of ZnO thin films were observed and analyzed. The films with suitable thermal nature were carefully chosen and ZnO thin film temperature sensor was fabricated. An electronic circuit was designed and constructed for ZnO thermometer and its performance was studied and analyzed.

1.2 LITERATURE SURVEY

ZnO is a widely used functional material with wide and direct band gap, large exciton binding energy, and excellent chemical and thermal stability [15]. ZnO is a semi-conducting material widely used as transparent electrodes in solar cells[16], chemical and gas sensors[17], spintronic devices[18], and light emitting diodes[19]. Different types of techniques for deposition of ZnO films have been reported, such as sputtering[20], spray Pyrolysis [21], chemical vapour deposition [22] and sol-gel method [23–27]. Nowadays, the sol-gel method has been extensively used to obtain various kinds of functional oxide films due to its simplicity and low cost. Fabricating high quality ZnO thin films on substrates and the analysis on its physical and chemical properties are important for the applications such as energy efficient windows, liquid crystal displays, opt - electronic devices, pies-electrical devices acoustic electrical devices, laser diodes and sensors. The ZnO is a good alternative candidate for ITO and analogous to GaN. Furthermore, bulk ZnO is quite expensive and unavailable in large wafers and for the time being, ZnO thin films are relatively a good choice.

Wang et al., [28] prepared ZnO film using aqueous/ethonolic solution of zinc acetate and showed that as-deposited films consist of nanocrystals with their orientation being tuned by varying the volume ratio. Dauli et al., [29] coated ZnO thin film on glass substrate, strong peak was obtained from (002) plane. Direct allowed transition was observed with an optical band gap at 3.29 eV. PL spectra were dominated by a strong luminescence peak in the yellow-green region at room temperature [29]. Wu et al., formed the ZnO film on glass substrate and films exhibited polycrystalline wurtzite structure. The optical band gap was 3.26 eV and the dark electrical resistivity was also studied [30]. Mizuta and Ishibashi [31] prepared ZnO film with zinc nitrate and
dimethylamineborane and films with a high crystal density with c axis orientation and high refractive index were obtained. Wang and Xie used Zinc nitrate and hexamethylene tetramine (HMTA) for film fabrication and a novel microsphere with nanometer holes separated by thin flakes and ZnO hierarchical structure with rod like branches were formed [32,33].

The ZnO thin films have been deposited using CBD by many researchers [34-38]. The effect of dopants such as Sn, Li, Al, Br on structural, optical and electrical properties of ZnO thin films has been studied [39-41]. The ZnO thin films are used for different application such as PEC solar cell, dye sensitized solar cell, gas sensors, thin films transistors [42-47]. Zhang and Kerr synthesized ZnO thin films with different morphologies. The CBD method offers a new opportunity for manipulating the morphologies of ZnO thin films by controlling the size and growth orientation of ZnO crystal, which has important applications in optoelectronic devices [48].

The hexagonal ZnO films composed of compact columnar grains with uniform size distribution have deposited on flexible stainless steel substrate by Rakhshani et al., [49,50]. The deposited films were highly oriented along the (002) direction normal to the substrate. Films exhibit photoluminescence at room temperature, which is the indication for the high optical quality. The as-grown films show PL emission at room temperature with a UV peak in the range $3.22 \pm 0.04$ eV (380-390 nm) and a broader peak in the visible region. The zinc hydroxychloride phase, which most likely is present in the films grown from Cl-containing solutions, suppresses the UV emission. Ghosh et al., [51] deposited hexagonal ZnO thin films on glass substrate and studied their structural, optical properties. The polycrystalline hexagonal ZnO films were successfully prepared at room temperature by Shinde et al., [52]. The reaction period affects the crystallinity, surface morphology and optical properties. Also Shinde et al., [53] studied the effect of surface morphology on the LPG sensing properties. The LPG sensing performance was enhanced significantly after Pd-sensitization to 57% at a relatively low operating temperature with a rapid response time of 15sec to a concentration of 0.4 vol.% LPG. Vaezi et al., [54] synthesized highly textured ZnO thin film with a preferred (002) orientation on glass substrate. Mitra et al., [55,56] deposited strongly c-axis oriented polycrystalline ZnO films in the thickness range 0.25-4.0 μm from ammonium zincate bath. The polycrystalline
and nanoporous ZnO film was deposited by Gao et al., [57,58] on glass and Si substrates. Al thin films were synthesized by Lupan et al., [59] on glass and Si substrates. The carbon dioxide sensitivity of Al-doped ZnO was improved by increasing surface to volume ratio of nanostructures. These experimental results confirm that gas sensors based on Al-doped ZnO as sensitive layer are of great interest for gas detection. ZnO thin films were synthesized on glass substrates by Hernandez et al., [60]. Crystallinity is favored for an increase in number of cycles because in the first cycles an amorphous layer is grown and later the material became higher ordering. ZnO:Sn and ZnO:Ni films have been deposited by Lupan et al., [61] on glass substrates. The gas sensing characteristics of the ZnO films were improved drastically by introducing Sn and Ni dopants into the sensing films.

The above review, we have presented recent status of

(i) chemical bath deposited (chemical bath deposition (CBD) and

(ii) successive ionic layer adsorption and reaction (SILAR) methods

The two methods are simple, inexpensive and convenient for large area deposition and capable of yielding nanocrystalline thin films. The metal chalcogenide and metal oxide thin films are technologically important in devices such as solar selective coatings, solar cells, photoconductive cells, photo electrochemical cells, dye sensitized cells, gas sensors, etc., where large area is desirable.

1.3. SCOPE OF THE PRESENT WORK

Even though a number of reports are available as seen in the previous section on the preparation and study of some physical properties such as structural, electrical and optical properties of chemical bath dip coated ZnO films, sufficient information are not available on the thermal behavior and also on ZnO as thermal sensor. We designed a simple, economical pc controlled dip coating machine specially meant for SILAR method. The purpose of the present work is to prepare ZnO thin films by employing our own dip coating machine. The SILAR method was used for the preparation of thin film samples with different adsorption rate and reaction rate. The prepared films were characterized and their physical properties such as structural and optical behavior were studied. The thermal behaviour the samples were studied to use them as a temperature sensor.
1.4. DETAILS OF THE PRESENT WORK

Chapter II discusses the details of design, fabrication of linear up/down motion control and rotating base. And the performance analysis such as noise figure, payload and power consumption were also discussed.

Chapter III deals with four experimental methods for the preparation of thin film samples by SILAR method by changing the adsorption rate and reaction rate.

Chapter IV is on the deposited weight, thickness obtained, the structural studies such as XRD, SEM and EDAX for samples prepared in all four methods.

Chapter V presents the thermal behaviour such as rate of resistance variation with temperature, resistance variation with time, temperature coefficient, resistivity and figure of merit of prepared of films in all four methods.

Chapter VI deals with fabrication of ZnO based thermometer and performance such as linearity and offset adjustments.

Finally the important conclusions drawn from the studies on ZnO films were summarized and presented in Chapter VII.

Part of results presented in this thesis has been published in the form of following papers.


References