

LITERATURE SURVEY AND SCOPE OF THE PRESENT INVESTIGATION

In this chapter an earlier work on the preparation and characterization of semi-conducting metal oxide thin films such as ZnO, Cu₂O, SnO₂ and Co₃O₄ are focused with the scope of the present investigation.

2.1. INTRODUCTION

The simultaneous benefit of high optical transparency (more than 80%) in the visible region and high electrical conductivity (about $\geq 10^3 \Omega \text{ m}^{-1}$) is not possible in an intrinsic stoichiometric material. Partial transparency and fairly good conductivity can be obtained in thin films of a variety of metals. The only way to obtain good transparent conductors is to create electron degeneracy in a wide band gap ($> 3 \text{ eV}$) oxide by introducing non stoichiometry and / or appropriate dopants. These conditions are conveniently achieved in oxides of cadmium, tin, iridium, zinc and their alloys prepared by a number of deposition techniques.

A host of electronic, opto-electronic and mechanical applications based on transparent conductors has emerged. These film devices include the following: resistors, transparent heating elements, aircraft and automobile windows, antistatic coatings for instrument windows, heat reflecting mirrors for glass windows and incandescent bulbs, and antireflection coatings, selective absorbs components in solar heat collectors, gas sensors, electrodes for liquid crystal display, electrochromic device and ferroelectric photoconductor storage and display devices etc...

Now it is possible to tailor make various transparent conductors with a range of properties. A maximum solar transmittance of about 85% - 95% with minimum

resistivity as low as about $7 \times 10^{-5} \Omega \text{ cm}$ is achievable and still further improvements in these parameters are expected to take transparent conductors into the semimetal regime.

Holland [1] reviewed the progress till 1955. Reviews by Vossen [2] and Haacke [3] discussed the developments till the mid 1970's. A brief review has been given by Manificier [4]. Major developments in this field regarding the deposition techniques, properties of the films thus obtained and their understandings have been covered [5-6].

2.2. EARLIER WORK ON ZnO THIN FILMS

Tang et al [7] have reported the deposition of transparent conducting aluminum doped ZnO thin films using a soft gel process. They also examined the dependence of electrical characteristics upon aluminum concentration in the films and the post-deposition heat treatment in vacuum. The effect of changing the aluminum to zinc ratio from 0.1% to 4.5% (atomic) and the heat treatment temperature in vacuum had been thoroughly investigated. Resistivities of $(7-10) \times 10^{-4} \Omega \text{ cm}$ had been achieved for ZnO/Al films with Al/Zn ratios of 0.8% at heated to 450 °C in vacuum. Transmittance in the visible region is above 90%. Similar results were obtained using aluminium chloride and aluminium nitrate as the aluminium precursor.

Masanobu Izaki et al [8] cathodically deposited ZnO thin film on NESA glasses from aqueous solution of 0.03 to 0.1 mol/lit of zinc nitrate solution at 335 K. The films had wurtzite structure and optical band gap energy of 3.3 eV which is characteristic of ZnO.

Kamalasanan et al [9] reported that the deposition of zinc oxide on four different substrates namely fused silica soda glass, silicon wafer and KBR single

crystals using the sol gel technique. A sol had been prepared by reacting zinc acetate and ethylene glycol and dissolving the resultant transparent brittle solid in dry n-propanol. Triethylamine was added as proton acceptor to assist the hydrolysis of zinc acetate. The resulting solution was readily gelled with the addition of water. The films were then spin coated on polished substrates, gelled in humid air and pyrolysed at 450 °C to get polycrystalline ZnO thin films. These films were characterized by using X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and visible absorption spectroscopy.

Alkaine et al [10] have developed a quantizing theory for better understanding of the potentiostic growth of passivating films on Zn in a mixture of 0.3 M H_3BO_3 plus 0.15 M $\text{Na}_2\text{B}_4\text{O}_7$ solution. The evolution of the ionic specific resistivity in terms of the existence of defect injection at the metal / film and film / solution interfaces was discussed.

Maganobu Izaki et al [11] reported that the preparation of grown transparent ZnO films by galvanostatically deposition onto conductive glasses from a simple aqueous solution of zinc nitrate electrolyte maintained at 335 K. The prepared ZnO films had a wurtzite structure and exhibited optical band gap energy of 3.3 eV which was characteristic of ZnO. At a low cathodic current density of 0.05 mA cm^{-2} , ZnO films with excellent electrical characteristic were obtained. A 2 μm thick ZnO film with an optical transmittance of 72% was deposited by electrolysis for approximately 20 min at cathodic current density of 10 mA cm^{-2} .

Sophie Peulon et al [12] electrodeposited ZnO films cathodically in aqueous ZnCl_2 solutions using dissolved oxygen as a precursor. The influence of the precursor concentrations on the growth, composition and properties of the films were investigated by means of in sites techniques.

Gu et al [13] deposited ZnO films on tin coated glass electrodes. The films were obtained at a low temperature by an electrolytic process. Jaeyoung Lee et al [14] co deposited Cu₂O and ZnO on indium tin oxide substrate and the formation mechanism of ZnO onto Cu₂O was investigated by X-ray, in-situ SEM, XRD and XPS. Gal et al [15] cathodically electrodeposited ZnO by reduction of dissolved oxygen in a non-aqueous solution containing a zinc salt. This method allowed a large deposition potential window and gave films with high transparency good crystallinity and adherence. Canava et al [16] electro deposited ZnO, thin film from oxygenated aqueous solutions of zinc chloride at 80°C on tin oxide covered glass substrates. The activation fragment formation was initially thin in the deposition solution of a thin metallic zinc layer (5 – 50 nm) which was then converted to ZnO by in-situ re-oxidation.

Thin films of ZnO were also prepared by a simple and inexpensive chemical bath deposition technique from zinc acetate precursor solution and films were annealed at 773 K for 2 hours. The resultant films were of good quality, structural, electrical and optical properties of the thin films were carried out [17]. Effects of the incorporated boron on the structural, optical and electrical characteristic of ZnO film were investigated using X-ray diffraction, followed by evaluation of surface morphology with an atomic force microscope, optical transmission spectra and Hall measurements. Small amounts of boron atoms which oriented from the DMAB were incorporated into ZnO grain and had the lattice expansion. A pore free ZnO film with a smooth surface was obtained from the 0.1 mol /L DMAB solution. The ZnO film showed optical transmission as high as 80% in the visible light region and resistivity of $3.6 \times 10^{-2} \Omega \text{ cm}$ and with carrier concentration of $1.7 \times 10^{16} \text{ cm}^{-3}$ and mobility of

$1.0 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. It was speculated that the incorporated boron atom acted as a donor in the ZnO film [18].

Yoshida et al [19] studied the electrodeposition of the ZnO / eosin δ hybrid thin films from aqueous mixed solutions containing $\text{Zn}(\text{NO}_3)_2$ and eosin y and they observed under the conditions of film preparation, electrochemical reduction of an eosin y molecule coupled with stable complex formation with Zn^{2+} ion. Pauporte et al [20, 21] deposited ZnO cathodically at 70°C from a chloride aqueous solution containing dissolved hydrogen peroxide and zinc chloride. The electrodeposition process was studied by cyclic voltammetry, chronomaperometry and quartz crystal microbalance techniques. The study was carried out by varying the solution composition and the substrate. A transition between dense films and porous films was observed at higher H_2O_2 concentration core investigated. In $40\text{mM H}_2\text{O}_2$, the porosity of the films deposited in the presence of 80 mM zinc per chlorate was estimated as 33% with deposition rate of $\text{Ca } 16\mu\text{mh}^{-1}$.

Dalchide et al [22] reported that the deposition of ZnO thin film onto nanocrystalline n-type Si (100) substrate by electrodeposition at different applied potentials. Optical measurements were made on the samples deposited on ITO/glass using the same procedures giving a band gap of 3.3 eV in agreement with the reported values for ZnO at room temperature. Lee et al [23] reported that the effect of the concentration of hydroxide ion adsorbed (OH) on indium tin oxide (ITO) in the electrodeposition of ZnO by potential modulation method. They found that by applying an optimal constant potential of -0.72V , X-ray diffraction peak intensity of crystalline phase indicating ZnO (101) and (101) deposited in oxygen containing solution was significantly higher than that of ZnO formed in oxygen free solution.

Pauporte et al [24] deposited zinc oxide thin film using dissolved hydrogen peroxide as the oxygen precursor and cathodic electrodeposition method. These films were deposited at 70 °C and – 1.4 V vs. saturated mercurous sulfate electrode onto tin oxide over a large range of peroxide concentration with perchlorate as the supporting electrolyte. These films were well covered and crystallized with wurtzite structure and textured with the co- axis perpendicular to the electrode surface. A transition between dense films and porous film was observed at the higher concentration of the hydrogen peroxide.

Brain O' Regan et al [25] electrodeposited nonporous ZnO films on transparent conductive supports using an electrolyte of LiNO₃ and ZnCl₂ in propylene carbonate (PC). The morphology and porosity of the films variation with salt concentration, water content and voltage were studied. The morphology of developed films was proven to be useful in constructing solid – state dye sensitized solar cells. Karuppuchamy et al [26] deposited zinc oxide and titanium dioxide thin film cathodic electrodeposition methods. They aimed to develop cost effective alternative rules to the photoelectrode materials for dye sensitized solar cells (DSSCs). They have also developed a sandwich cell using the electro deposited ZnO/N₂ film photoelectrode measured $I_{sc} = 0.61 \text{ mA/cm}^2$, $V_{oc} = 0.46 \text{ V}$, $F.F = 0.46$ and $n = 0.13\%$ under illumination by an artificial light source, being the first example of a real working DSSC fabricated without any heat treatment.

Natsume et al [27] prepared doped and undoped ZnO thin films by sol gel method. The undoped films were post annealed in hydrogen at 350 °C for three hours followed by annealing from 500°C – 575°C. The chemical and optical properties were investigated and presented the following values were given film

resistivity 0.22Ω , optical band gap value $E_g = 3.20 - 3.21 \text{ eV}$ and wide of the localized state $E_e = 0.08 - 0.09 \text{ eV}$.

Jeyakrishnan et al [28] electrodeposited ZnO films from a dimethyl sulfoxide bath containing dissolved gaseous oxygen. Variation in deposition parameters and their effects on the structural (crystal size, growth direction) optical (band gap variations, photoluminescence) and electrical (conductivity) properties were studied.

Sukasa Yoshida et al [29] reported that electrode position of ZnO /eosin y hybrid thin films from aqueous mixed solutions of zinc chloride and eosin y as promoted by the reduction of oxygen. Highly oriented crystalline hybrid films with two distinctive structures were obtained depending on the redox state of eosin y. Deposition at potentials more positive than that of eosin y reduction resulted in the formation of compact ZnO crystals into which eosin y molecules were entrapped while that accompanied with the reduction of eosin gave a film consisting of sponge structure of ZnO crystals with internal nonporous structure to which eosin y molecules were absorbed. The addition of eosin y accelerated the film growth both in oxidized and reduced forms due to its catalysis toward the reduction of oxygen.

Jin Hong Lee et al [30] reported the effect of drying conditions and the first and second heat treatments on the structural electrical and optical properties of ZnO thin films prepared by the sol gel spin coating method on silica glass substrates. Zinc acetate dihydrate, 2-methoxyethanol and monoethylamine were used as a starting material, solvent and stabilizer, respectively. The films had (002) plane as more preferment orientation. Optical transmittance was higher than 85% in the visible region and the resistivity value was $0.099 \Omega \text{ cm}$.

Yoshida et al [31] studied the mechanism of electrodeposition of zinc oxide (ZnO) thin films from aqueous solution of zinc nitrate under controlled mass transport

by using a rotating disk electrode. They showed that the improvement of the electron transfer kinetics. The catalytic role of Zn^{2+} ion to the reduction of nitrate was discussed. The current in the presence of Zn^{2+} at various concentrations was described by Langmuir isotherm of Zn^{2+} catalysts to the surface sites of ZnO for which an equilibrium constant of $1.23 \times 10^5 \text{ cm mol}^{-1}$ was obtained.

Ramamoorthy et al [32] deposited highly textured zinc oxide (ZnO) thin films with a preferred (101) orientation from chemical bath deposition using sodium zincate electrolyte on glass substrates. The films were characterized by SEM, EDAX, optical FTIR and photoluminescence spectroscopy. Gao et al [33] reported a novel and simple chemical method for the deposition of zinc oxide films from aqueous solution, integrating the merits of successive ionic layer adsorption and reaction with the chemical bath deposition technology. By this new method dense and continuous ZnO thin films were prepared in a very short time i.e., in about 20 min. The film exhibited hexagonal wurtzite crystalline structure and the preferential orientation along (002) plane and the films possess high optical quality.

Ranjani Viswanatha et al [34] reported that the synthesis of high quality nanocrystals with sharp absorption edges in four different sizes namely 3.0, 3.5, 4.7 and 5.4 nm and characterized them by X-ray and electron diffraction and transmission electron microscopy. Marotti et al [35] reported that the electrochemical deposition of zinc oxide thin films onto opaque and transparent substrates (copper and ITO coated glass). The electrolyte consisted of a 0.1 $mZn(NO_3)_2$ solution with the initial pH was adjusted to 6.0 and with different electrodeposition potentials from $E = -700$ to -1200 mV (SCE) . The resulting samples had the structural, chemical and morphological properties of hexagonal ZnO, with

thickness varying from less than 1 μm to almost 30 μm . The band gap energy varied inversely with film thickness, ranging from less 3.1 to 3.4 eV.

Torsten Oekermann et al [36] reported the self-assembled growth of ZnO films modified with N, N' bis (ethelylene sulphate) 3, 4, 9, 10, propylene tetra carboxylic acid diimide (SO_3 ETPtCDI). Scanning electron microscopy and X-ray diffraction examination in the ZnO / SO_3 EtPTCDI hybrid films had been revealed that the morphological and structural changes increased with dye concentration in the deposition bath.

Goux et al [37] studied a thermo chemical study on the ZnO.H₂O system by means of potential/pH solubility and the species repartition diagrams was presented with the view to better understand the effect of temperature on the deposition mechanism and composition of zinc oxide thin films. The calculations completed on film preparation at different temperatures between room temperatures and 90 °C below which they pointed out the absence of continuous film growth and surface passivation. The oxide nucleation and film growth started above 34 °C whereas the optimum film transparency and crystallinity were obtained at temperature 40°C.

Hly et al [38] deposited ZnO films grown on polycrystalline zinc foil by cathodic electrodeposition in an aqueous zinc chloride solution at 80 °C. They observed a variation in the electrochemical parameters with growth morphology. Huai Yu Jing et al [39] reported that highly oriented zinc oxide surfactant hybrid multilayer deposited electrochemically on silicon substrates from $\text{Zn}(\text{NO}_3)_2$ solution containing extremely low concentration of sodium dodecyl sulphate (SDS). They also showed that the X-ray diffraction results were sensitive (films morphology) to the concentration of SDS by means of film morphology.

Zhifeng Lin et al [40] prepared ZnO on glass substrates by sol gel method with polyethylene glycol (PEG) as organic template, zinc acetate dihydrate as precursor, ethanol as solvent and $\text{NH}(\text{C}_2\text{H}_2\text{-OH})_2$ as chelating agent. The films were characterized IR, TG-DTA and SEM. The physiochemical changes occurred during sol gel process. Effects of zinc acetate dihydrate concentration, PEG content and water bath temperature on the characteristics of the films were discussed. The films morphology of porous ZnO thin films strongly depended on these processing factors.

Jun Liu et al [41] described highly oriented zinc oxide thin films and having resistivity value suitable for great potential piezoelectrical devices. Li, Mg doped ZnO on glass substrate by sol gel spin coating method was prepared. The dopants effects and heating temperature on C-axis orientation and resistivity of the resulting films were investigated. They showed that the Mg doping into Li ZnO films improved C-axis orientation and increased the resistivity of the optimized (Li, Mg): ZnO film. They had highly C-axis orientation, small grain size and resistivity of $11.18 \times 10^7 \Omega \text{ cm}$.

Mridha et al [42] reported a series of their work on zinc oxide thin films with different thicknesses on glass substrates by utilizing sol gel techniques. By varying the spinning frequency films thickness, the structural, electrical and optical properties were investigated. From XRD data FWHM of the (002) diffraction peak and the strain along C-axis were developed as the film grew up to a thickness of 300nm. Above 300nm, strain became appreciable. Electrical resistivity results showed that ZnO film with thickness of around 260 nm had highest resistivity.

$\text{Zn}_{1-x}\text{Co}_x\text{O}$ films were grown on glass substrate by sol gel spin coating. The coated films with 10% Co were highly C-axis oriented the electrical resistivity of the films was low due to the highest C-axis orientation. XPS and AEM analyses indicated that Co metal clusters were not formed and the ferromagnetism appeared

at room temperature. The electrical resistivity and room temperature ferromagnetism values of the films suggested that it could be used as a potential application to dilute magnetic semiconductor devices [43].

Vaezi et al [44] deposited Sn – doped ZnO films from a zinc complex solution containing tin ions onto Pyrex glass substrates using a two – stage chemical deposition (TSCD) process. The experimental results showed that the deposition rate was increased linearly with Sn concentrations (atomic percent) when lower than 3% of them were used. Only the (002) X-ray diffraction 2θ peak appears in the range of this study. The incorporation of tin atoms into zinc oxide films was obviously effective, when Sn concentration was above 2.5%. The resistance of undoped ZnO films was high and reduced to a value of $4.2 \times 10^{-2} \Omega \text{ cm}$ when 2.5% of Sn was incorporated. All of the zinc oxide films had $> 80\%$ transmittance in a range of 400-700 nm. The optical energy gap increased with the amount of Sn in the ZnO films.

Bhattacharyya et al [45] studied the preparation of nano crystalline zinc oxide thin films derived by sol-gel method for the fast response methane sensors. The response time and recovery time were studied in detail. Zinc (2+) ion implantation to a dose of $1 \times 10^{17} \text{ ions/cm}^2$ was performed on ZnO thin films deposited on silica glass substrate by the sol gel technique. The films were annealed in air at different temperatures from 500 – 900 °C. The effects of ion implantation and post thermal annealing as the structural and optical properties of the ZnO films were investigated by X- ray diffraction (XRD), photoluminescence (PL) and optical absorption measurements. XRD data revealed that the diffraction peaks recovered at $\sim 700 \text{ }^\circ\text{C}$. Optical absorption measurements showed that the absorption edge blue shifts when the annealing temperature is below 600°C while red shifts when the annealing at above 600 °C was reported by Xue et al [46].

Robles et al [47] developed Thorpe's formula for the effective electrical conductivity of elliptical holes randomly distributed in a matrix to a system composed of conducting ellipses in a conducting matrix. This was applied to the electrical conductivity of chemically deposited polycrystalline ZnO thin films. They compared the calculated values and experimented results obtained by two different deposition methods and spray pyrolysis. Successive ion layer adsorption and reaction (SILAR) were also reported.

Srinivasan et al [48] reported the deposition of zinc oxide by thin layer sol gel spin coating techniques onto (0001) sapphire substrate and characterized them by X-Ray diffraction method, UV emission and photoluminescence spectra. Sea-Fue Wang et al [49] studied the effect of ZnO seed layers on the solution chemical growth of ZnO nanorods arrays. The uniformity and alignment of the nanorods arrays were strongly related the properties of underneath ZnO seed layers.

Jianguo Lu et al [50] studied the nanostructured ZnO thin films deposited on Si (111) and quartz substrate by sol-gel method. The thin films were annealed at 673K, 873K and 1073K for 60 min. Wettability results indicated the hydrophobic nature of the un-irradiated ZnO thin films which improved with annealing temperatures. Jianguo Lu et al [51] reported the Na-doped ZnO thin films with different Na/Zn ratio prepared by sol-gel method. The relation of wettability and Na/Zn ratio was been studied.

Gurav et al [52] prepared thin films of ZnO on glass substrate by soft chemical deposition route at room temperature. He found that annealing at 400°C removed zinc hydroxide phase and nanofibrous ZnO films with wurtzite crystal structure. Tarwal et al [53] prepared transparent and super hydrophobic ZnO thin film by a simple spray pyrolysis technique onto the glass substrate at 723 K from an aqueous

zinc acetate precursor solution. He found that the sample shows the optical gap of 3.25 eV.

Lupan et al [54] prepared ZnO thin films by electrodeposition in chloride medium. The improved its optical quality by post deposition thermal treatment at 150°C and 400°C. These ZnO thin films have potential for the growth of high quality ZnO thin films with reduced defects for device applications. Jianguo et al [55] studied the effect of annealing temperature on photocatalytic activity of ZnO thin films prepared by sol-gel method.

Tarwal et al [56] studied the enhanced photoelectrochemical performance of Ag-ZnO thin films by spray pyrolysis technique. He found that the optical band gap energy decreased as the Ag doping increased. Tari et al [57] prepared ZnO transparent and conductive films by sol-gel method. They examined structural, optical and morphological characteristics of the films.

Mammah et al [58] studied the effect of concentration on the optical and solid state properties of ZnO thin films deposited by aqueous chemical growth method for various optoelectronic applications including its application as absorber layer in solar cells.

2.3. EARLIER WORK ON Cu₂O THIN FILMS

Now-a-days much interest is given to the development of low cost energy producing devices. Cuprous oxide is a potentially useful material for photovoltaic cells because of its favorable band gap energy range of 1.9 – 2.1 eV. Cu/Cu₂O layered nanostructured materials prepared by electrodeposition had interesting optoelectronic properties.

Cu₂O acts as a stable photo catalyst for the photo chemical decomposition of water into O₂ and H₂ under visible light irradiation. Cu₂O thin films possess good optoelectronic properties. Cu₂O was prepared by oxidation of copper in air at higher temperature.

Stareck et al [59] electrodeposited Cu₂O films. Bardeen et al [60] deposited Cu₂O and found that a decrease in resistivity of the film was achieved by the creation of more copper ion vacancies. Measurements on dislocation density of Cu₂O thin films were made [61].

Pastrynyake et al [62] carried out studies on optical properties and measured the absorption coefficient values for Cu₂O and reported the values are 10⁴ cm⁻¹ at $\lambda = 0.5\mu\text{m}$. Weichman et al [63] studied optical properties of cuprous oxide and estimated the band gap value as 2.0 eV. Abrupt decrease in photo response of back wall single crystal due to intrinsic absorption of light by Cu₂O was reported elsewhere [64]. The crystal structure of Cu₂O was studied and it has cubic structure with a lattice constant value of 0.427 nm.

Scottky et al [65] prepared Cu₂O/Cu contact and estimated the diffusion potentials for Cu₂O/Cu contents. Films with a high concentration of copper vacancies prepared by of oxidation of copper at 1100 °C showed extremely high absorption greater than 10⁴ cm⁻¹ in the tail region. This strong tail effect was due to Cu ion vacancies [66]. Lawless et al [67] studied the deposition of Cu₂O on Cu substrate and determined that the deposition on (100) plane produced four-sided pyramid where as deposition on (111) plane had three-sided pyramid. Excitation and emission spectra of Cu₂O thin films at 1.6 K were reported [68].

Warren et al [69] calculated the values of coherent domain size, RMS, microstrain and dislocation density of as deposited and annealed Cu₂O films.

Specific heat capacity “Cp” of Cu₂O thin films was deduced [70]. Ladelfe et al [71] studied the optical properties of Cu₂O and reported the values of extinction coefficient “K” of as-deposited Cu₂O film.

Fitzgibbon’s et al [72] predicted the importance of various deposition techniques in construction of solid-state devices and in the applications of integrated circuits. Gruy et al [73] reported the method of preparing polycrystalline growth method. Assimos et al [74] carried out annealing studies and reported that annealing at 500 °C was optimum for producing higher, conductivity in large crystals.

Mitra et al [75] considered the errors in the series expansion of a logarithmic function of transmission and showed that a plot of $\ln T$ vs $1/d^2$ was non-linear. Studies on emission spectra were carried out and the reasonably intense emission bands at 175 and 200 K were reported [76]. A detailed analysis of one-dimensional theory of photoacoustic effect of solid was proposed [77]. Adams et al [78] reported the measurement of thickness of Cu₂O film using thermal diffusivity method.

Economic et al [79] fabricated Cu₂O thin film by electrodeposition method and used Cu₂O thin film for the fabrication of photovoltaic devices. Sharma et al [80] reported that Cu₂O thin film behaved as an active solar cell material, selective solar absorber layer and oxygen or humidity sensor. Olsen et al [81] fabricated low cost material and constructed solar energy conversion devices based on these materials. Electrochemical deposition of Cu₂O thin films using different bath solutions was studied [82]. Electrical properties characteristics of the diodes have been reported [83].

Potclar et al [84] prepared of Cu₂O thin films for solar selective coatings. Deposition of Cu₂O thin films by thermal oxidation technique and their characterization was reported [85]. Extensive studies on Cu₂O Schottky barrier solar

cells have been conducted [86]. Optical properties of Cu_2O thin film were studied and the emission spectra at 24 K were reported elsewhere [87]. Study on Cu_2O as active layer in various types of solar cells was reported [88].

Sears et al [89] developed Cu_2O photovoltaic junction by the anodic oxidation of copper and studied the photovoltaic properties of Cu_2O thin film. Indium tin oxide/cuprous oxide photovoltaic cell was constructed and the results were reported [90]. For measuring thickness of Cu_2O films using optical interferometer method such as ellipsometry was developed [91]. Mandelis et al [92] measured thickness of Cu_2O films using PAS. Preparation of cuprous oxide thin film and its spectral measurements were done [93].

Resistivity values of Cu_2O thin films developed by chemical deposition technique were reported [94]. Profile fitting methods and integral breadth methods were used to evaluate the crystallite size, RMS, micro strain and dislocation density of Cu_2O thin films were predicted elsewhere [95]. The values of refractive indices of Cu_2O which were necessary for the calculation of β were measured [96]. Studies on annealing effect of copper and oxygen vacancies in cuprous oxide films by low temperature luminescence was reported [97].

Rakhshani et al [98] reported the uses of Cu_2O for solar energy conversion. Preliminary results on galvanostatic mode of deposition and results on the structure of the films were also reported [99]. Measurement of dispersion at low wavelength region in Cu_2O thin film was reported [100]. Galvanostatic deposition of Cu_2O thin films on stainless steel substrate was carried out and XRD pattern of the films were reported [101].

Deposition of cuprous oxide thin films by anodic oxidation of copper was reported [102]. Rai et al [103] reported that p-type cuprous oxide thin film deposited

at low temperatures followed by its optical and electrical properties, which differed from those prepared by high temperature oxidation techniques.

Potentiostatic electrodeposition of cuprous oxide was given [104]. Studies on conductivity of Cu_2O thin film, its temperature dependence and its thermo stimulated characteristics were reported. Potentiostatic deposition of Cu_2O on copper substrate was carried out and the studies on growth kinetics and structure were reported [105]. The behaviour of $\text{Cu}_2\text{O}/\text{Cu}$ contact as tunnel diode and its dependence diode on quantum mechanical tunneling were reported [106].

Extensive studies on Cu_2O Scholkey barrier solar cell have been conducted and the result of efficiencies of front wall and base wall cells and the effect of sulphidation had been reported. The photoelectrochemical characteristics of n-type Cu_2O films and the effect of sulphidation on photocurrent were given elsewhere [107]. Cuprous oxide (111) crystals prepared at 65°C in pH 4.7 by electrodeposition.

Galvanostatic deposition of a Cu_2O thin films and its electrical characterization was reported [108]. Evaluation of crystallite size RMS microstrain and dislocation during of Cu_2O thin films were also carried out [109]. Connel et al [110] described a method for the determination of optical absorption coefficient " α " at various photon energies. Snoke et al [111] reported that the Bose – Einstein condensation of excitons occur in Cu_2O at relatively high temperatures. Optical and electrical properties of cuprous oxide were studied [112]. Transmission of light through a nanometer scale aperture of Cu_2O without diffraction losses was reported [113].

Siripala et al [114] reported about annealing effects on cuprous oxide thin films grown by electrodeposition technique and also the effect of annealing on structural and optical properties. Santra et al [115] reported coherent domain size RMS, micro strain and dislocation density of as deposited and annealed Cu_2O films.

Switzer et al [116] reported that the layered nanostructure multilayers electrodeposition by pulsing the applied potential or current during growth. Wijesundara et al [117] studied about the characteristics of PEC cell based on Cu_2O and reported that the output of PEC cell could be improved by sulphiding the films. Fabrication of photoelectrochemical cell with higher energy conversion efficiency was reported [118]. It was observed that shifting of optical absorption edges were due to quantum confinement of carriers [119].

Fang Sun et al [120] studied on cuprous oxide (Cu_2O) thin films were formed by cathodic deposition of cuprous acetate. They reported the influence of additive on crystal morphology of Cu_2O and changes in morphology by addition of simple salts. Kajari das et al [121] reported the preparation of Cu_2O by solvothermal and UV-Visible absorption study. Liangbin Xiong et al [122] synthesized Cu_2O films by CBD technique. Liangbin Xiong et al [123] reported the cuprous oxide thin film by solvothermal method using acetate aqueous solution. The photoelectrochemical experiments on the Cu_2O thin films showing both n-type and p-type semiconductor characters.

Partha Mitra [124] synthesized polycrystalline thin film of copper oxide by successive ionic layer adsorption and reaction (SILAR) technique. The author exempted to fix the concentration of anionic precursor (1.0 M KOH) and concentration of copper sulphate complex. For lower concentration, mixed phase of CuO and Cu_2O was found. Phase pure Cu_2O was observed with enhanced concentration of cationic precursor.

Hari Prasad Reddy et al [125] prepared cuprous oxide thin films deposited on glass substrates by sputtering of copper target at different temperatures and at oxygen partial pressure using RF-magnetron sputtering method. They investigated

the prepared Cu_2O thin film properties. Ahirrao et al [126] prepared Cu_2O thin film on amorphous glass substrate by using simple chemical route namely, modified chemical bath deposition method at room temperature and reported the photoluminescence properties of copper oxide thin film.

Du et al [127] developed a simple electrochemical deposition method to prepare cuprous oxide on aluminum foils and studied the formation mechanism. Rachel Oommen et al [128] deposited cuprous oxide thin films (Cu_2O) on glass plates by electron beam evaporation of Cu_2O powder and electrodeposition. These results reveal that the electrodeposited and electron beam evaporated cuprous oxide thin films were suitable for photovoltaic and gas sensor applications, respectively.

Kasim Uthman Isah et al [129] prepared copper thin films on glass substrates using thermal vacuum evaporation at $100\text{ }^\circ\text{C}$ substrate temperature and then thermally oxidized in air at varying temperatures of $150\text{ }^\circ\text{C}$, $250\text{ }^\circ\text{C}$, $350\text{ }^\circ\text{C}$ and $450\text{ }^\circ\text{C}$ for 2 h each. They found the formation of fine grain cuprous oxide (Cu_2O) at $250\text{ }^\circ\text{C}$ and cupric oxide (CuO) at 350 and $450\text{ }^\circ\text{C}$.

2.4. EARLIER WORK ON SnO_2 THIN FILMS

Tin oxide, (SnO_2) is the first transparent conductor to receive significant commercialization. In 1937 tin oxide semiconductor film prepared by thermal action on quartz substrate in oxygen atmosphere was reported [130]. This received attention after 1940. Marton [131] reviewed the progress after the year 1940.

Optoelectronic properties of tin oxide were summarized [132]. A detailed survey article described the status and technical application of tin oxide, indium oxide and cadmium oxide [133]. The scientific information on the conductivity and optical transparency, dependence of electrical and optical properties of starting

materials, deposition parameters and areas of application till 1975 is known. In this series, Z.M. Jarzebski surveyed up to 1982 and gave physical properties and the deposition methods of SnO_2 , In_2O_3 , Cd SnO_4 and $\text{In}_2\text{O}_3 : \text{Sn}$. An exhaustive review on the methods of preparation and the electrical and optical properties of $\text{SnO}_2: \text{F}$, In_2O_3 and $\text{In}_2\text{O}_3 : \text{Sn}$ films by surveying the literature upto 1982 was given [134].

Paulo Olivi et al [135] proposed a method of preparation of SnO_2 thin films. The films had reversible electrochemical insertion of lithium ions while maintaining high optical transmissivity. Yoo et al [136] prepared SnO_2 thin film from tin oxide sol by spin coating to sense hydrogen sulfide gas on a quartz crystal substrate. Scanning electron microscopy and transmission electron microscopy were used to study its morphology.

Mirazzoni et al [137] studied Pt – doped and undoped nanostructured tin oxide thin films by sol- gel method using tetra (tert – butoxy) tin (IV) and bis (acetylacetonato) Platinum (II) as metal precursors. The films were characterized not only by glancing incidence X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS) but also by Electron paramagnetic resonance (EPR) techniques.

Li et al [138] reported antimony doped tin oxide thin films from ethanol suspensions of Sb- doped SnO_2 nano particles by spin-coating process on Corning 7079 glass and the Hall mobility, μ , the carrier concentration, n , the sheet resistance, R , and the transmission spectra of the films were measured. Mn doped SnO_x thin films were fabricated by extended annealing of Mn/ SnO_2 bilayers at 200 °C in air for 110 hrs. By controlling the dopant concentration, the thickness variations of the films were studied. The overall thickness of the film was 115nm with dopant concentration between 0 and 30 wt% Mn. The films were characterized by X – ray diffraction UV transmission and AFM. Highest transmission observed in the films was 75% and

band gap values varied between 2.7eV and 3.4 eV. The presence of Sn interstitials rather than oxygen vacancies alone in the presence of Sn^{2+} was reported [139].

Indium tin oxide, (ITO) films containing different In: Sn atomic ratios, (Viz. 90:10, 70:30, 50:50, 30:70) deposited on two types of substrates namely i) sodalime silica glass, ii) silica films covered sodalime glass by sol – gel spinning technique. XPS analysis of the films was done. The narrower spectra obtained for the Na 1s, In 3d, Sn 3d and O 1s was reported [140].

Tin oxide, lead oxide (PbO) was prepared, using the spin coating technique. The influence of the temperature and duration of the thermal treatment on the final film composition were analyzed. The metallic oxide films were characterized by means of XRD, SEM/EDS and cyclic voltammetry. The electrochemical studies showed that the films were stable and was used as electrodes. Finally the films were tested as electrodes for the electrochemical degradation of a chloroform aqueous solution [141].

Highly transparent tin oxides thin films (SnO_2) were prepared by using sol-gel spin coating technique. Optimizing process parameters such as the solute concentration, spin rate and time of the turn table, film thickness and heat treatment temperature were studied. X-ray diffraction, studies pointed the polycrystalline structure of the developed film. The films deposited under optimum conditions were highly transparent in the visible region with a transmittance of 94% at 550 nm and had a resistivity of $3 \times 10^{-2} \text{ sLcm}$. The films were obtained at 400°C [142].

Baker et al [143] reported that the preparation of mixed metal oxide of stannates by sol-gel methods onto titanium substrates. Metal oxide such as Sb_2O_5 , ZnO_2 , CuO , MnO_x and PdO were introduced into a SnO_2 host matrix using sol-gel technology. The films were characterized for their chemical composition. TGA, SEM,

AFM and X-ray emission methods were also used. Zinc doped tin oxide films were prepared by using sol-gel spin coating process. The SnO₂: Zn multi coating films were deposited at optimum conditions using hydrochloric acid solution containing stannous chloride and ZnCl₂. Films with three coatings showed minimum sheet resistance of 1.479 K ohm/ cm² in the case undoped SnO₂ and 77 K ohm/ cm² for 5% Zn doped SnO₂ when coated on glass substrates were used.

Patil et al [144] reported the synthesis of tin oxide thin films by spray pyrolysis. The temperature effects on crystallinity and electrochromic performance were studied. The preparation of fluorine doped tin oxide via spray pyrolysis technique was made [145]. The effect of spraying solution quantity on the film thickness and growth rate was studied. Querfelli et al [146] prepared of fluorine doped tin oxide by chemical spray pyrolysis. Dengkui Miao et al [147] studied the effect of substrate temperatures on the crystal growth orientation of SnO₂: F thin films spray-deposited on the glass substrates. The lowest sheet resistance of 4.0 Ω was obtained with moderate optical transmission up to 75%.

Takeshi Ohgaki et al [148] synthesized SnO₂ thin films using pulsed laser deposition (PLD) method on silica glass substrates. They investigated their structures, electric properties and sensor performances of the films for NO₂ and H₂ gases respectively in air. Wang et al [149] prepared B₂O₃-doped SnO₂ thin film by combining electrodeposition and hydrothermal treatment and investigated its structure and electrochemical properties. They found that the as-prepared and modified SnO₂ film shows a porous network structure with large specific surface area and high crystallinity.

Etre et al [150] prepared SnO₂ thin film by cathodic electrodeposition. The obtained SnO₂ thin film has a tetragonal rutile crystal structure with large surface

area. Damrongsak et al [151] prepared SnO₂ thin films on borosilicate glass slides by ultrasonic spray pyrolysis method. In order to use these films as sensor, the sensitivity, response time and recovery time were improved for selective ethylene detection. Patil et al [152] prepared nanocrystalline SnO₂ thin films with size smaller than 10nm using a simple and inexpensive ultrasonic spray pyrolysis method. in to use as sensors material for high performance ethanol.

Parsanwale et al [153] prepared hydrous tin oxide (SnO₂·H₂O) thin films at room temperature by successive ionic layer adsorption and reaction (SILAR) method. The prepared thin films were hydrophilic in nature with semiconducting electrical behaviour. Carvalho et al [154] prepared the pure SnO₂ films by the sol-gel dip-coating, on glass, quartz, and silicon wrapper and studied their optical, electrical and structural properties. Sumanta Kumar Tripathy et al [155] prepared semiconducting SnO₂ thin film on a glass substrate using Tin (II) chloride as the precursor and methanol as solvent by dip coating method and optical properties was studied by Elco-UV/VIS Spectrophotometer.

Mohammed et al [156] prepared thin film of SnO₂ onto glass substrates at room temperature using thermal evaporation technique and observed its optical properties and band gap energy at 250 °C. He also found that the optical and morphological property of thin films decreased with increase of the annealing time. Dan Leng et al [157] prepared SnO₂ on borosilicate by RF magnetron sputtering using SnO₂ ceramic disc. The property of SnO₂ films have been investigated to obtain relatively high-resistivity which could be used as buffer layers to optimize the performance of CdTe/CdS solar cells.

Rafael Alvarez et al [158] prepared SnO₂ and ZnO films by magnetron sputtering on silicon and soda lime glass substrates. The films were characterized

and their properties were studied. Anjali Sharma et al [159] prepared tin oxide thin films of 430 nm thickness using RF sputtering technique on Pt inter digital electrodes (IDEs) patterned over the corning glass substrates using a tin metal target (99.999% pure) in a reactive ambient of Ar and O₂ for NO₂ gas sensing response characteristics.

2.5. EARLIER WORK ON Co₃O₄ THIN FLIMS

Cobalt oxide is one of the promising transition metal oxide materials which have many industrial applications such as solar selective absorber [160-161], catalyst in the process of crude fuels, pigment for glass and ceramics [162]. Varkey et al [163] reported the deposition of cobalt oxide thin films. CoO(OH) films were insulating and have DC dielectric break down at about 3700/mm. Electrical resistivity of Co₃O₄ 1.65 eV was calculated from UV absorption spectrum.

Cobalt oxide is also widely used as an electrochromic material reported by Fonseca et al [164]. The electrochromism in cobalt oxide thin films grown by anodic electrodeposition and the electrochromic efficiency, optical constant, durability, optical memory were studied. A facile preparation for the precursor complex and its characterization was reported [165]. Enrique Barrera et al [166] electrodeposited cobalt oxide on stainless substrate of approximately of 2.5 mm. Castro et al [167] reported the preparation of cobalt oxides through anodic depositions from cobaltous nitrate solutions on different substrates. The electroformed oxide films exhibited good chemical stability and lower oxygen over voltages, irrespective of the substrate material. Electrocatalytic properties were investigated through polarization curves and impedance measurements and the active surface area was estimated by cyclic voltammetry. The electrochemical formation of spinal-type cobalt oxide was

presented in which the potentiostatic or potentiodynamic oxidation with Au or Pt electrode in a solution of higher pH containing Co_3O_4 and glycine. A study on the electrochemical quartz crystal microbalance revealed that the electrodeposition of cobalt oxide preceded though the electrochemical oxidation of cobalt – glycine complex at a higher pH.

Enrique Barrera et al [168] prepared cobalt oxide thin films by dipping sol-gel process, using two different inorganic precursors. The thin films of cobalt oxide were characterized by means of X-ray diffraction, Ultra violet transmission spectra and atomic force Microscopy (AFM). The absorption coefficients higher than 10^4 were found for all the samples. Refractive index varied from $n \approx 1.9 - 2.8$ in the near IR region. Han-Ki-Kim et al [169] reported the electrochemical and structural properties of cobalt oxide films. The films were deposited at different sputtering gas ratio of $\text{O}_2 / (\text{Al}_2\text{O}_3)$. The capacitance behavior of films was similar to that of bulk type super conductor. X-ray diffraction and electrical results for the Co_3O_4 films were given. The cobalt oxide thin films electrodeposited, anodically consisted of cobalt oxide and cathodically of $\alpha\text{-Co}(\text{OH})_2$, $\beta\text{-Co}(\text{OH})_2$ and CoO respectively.

Lidia Armelao et al [170] prepared Co_3O_4 and other metal oxides taking cobaltous acetate as precursors. Tzintle et al [171] prepared sol-gel derived coatings containing cobalt and analyzed using impedance and reflection measurements. The electrochemical deposition and properties of cobaltous oxide in citrate alkaline solutions were carried out elsewhere [172]. The electrochemical behaviour of the electrodeposited cobalt oxide hydroxide film in alkaline solution and in the presence of various organic molecules was also investigated. The very fine cobalt oxide sol-gel powders were prepared using sol-gel process. The effect of thermal treatment on the surface area, pore volume, crystallinity, particle structure and corresponding

electrochemical properties of the resulting xerogels were investigated and found to have significant effects on all the above properties.

Hidero Unuma et al [173] reported the preparation of Co_3O_4 thin films by a modified chemical bath deposition method. Cobalt oxide thin films were deposited onto bare and ITO coated glass substrates at low temperatures. The reaction occurred were slow oxidation of Co (II) ion with BrO_3^- in to Co^{3+} ion and subsequent spontaneous hydrolysis to form a Co_3O_4 . The thin films consisted of particles less than 100 nm in diameter with low crystallinity and showed electrochromism. Mc Nally et al [174] cathodically electrodeposited cobalt oxide films using polyelectrolytes. The composite deposits were studied by SEM, and atomic force microscopy, X-ray diffraction and thermogravimetric analysis.

Barrera et al [175] deposited cobalt oxide and tin oxide films by the sol-gel process. This was to prepare selective photothermal coatings for medium temperature applications by superimposing those of cobalt. The films were studied by X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), and spectral measurement. Xia et al [176] prepared highly porous cobalt oxide thin film on ITO glass by a facile chemical bath deposition method. The film was characterized by cyclic voltammetry and chronomaperometry.

Xia et al [177] prepared self- supported Co_3O_4 nanowire array film by a facile thermal oxidative decomposition and its fast electrochromic properties. The Co_3O_4 nanowire array film exhibited a transmittance modulation of 32% in the visible region and fast response times with 18s for coloration and 1.45 for bleaching. Yanhaai Li et al [178] synthesized Co_3O_4 thin film on ITO by a chemical bath deposition. Co_3O_4 thin film exhibited a maximum specific capacitance of 227 Fg^{-1} at the specific current of 0.2 Ag^{-1} . The specific capacitance was reduced 152 Fg^{-1} and specific current

increased to 1.4 Ag^{-1} . The specific capacitance retention ratio was 67% of the specific current range from 0.2 to 1.4 Ag^{-1} .

Juan Xu et al [179] prepared the cobalt oxide (Co_3O_4) nanotubes by chemical deposition method using anodic aluminum oxide (AAO) templates for supercapacitor application. Yanhua Li et al [180] prepared Co_3O_4 thin film on ITO by a chemical bath deposition. They reported the chemical bath deposition provides a simple and available method to prepare transition metal oxide thin films for electrochemical capacitors. Akimasa et al [181] prepared cobalt and cobalt oxides on Si substrates from aqueous cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] powder by chemical vapor deposition method.

Shelkeet et al [182] prepared Co_3O_4 films using a two step method. The cobalt based films using electrochemical deposition method. They reported that the variation in molar concentration of CoCl_2 in electrochemical deposition bath showed the profound effect on optical properties of Co_3O_4 films. Vikas patil et al [183] prepared nanosized Co_3O_4 thin films on glass substrates by sol-gel spin coating technique. The Co_3O_4 films were annealed for various temperatures between $400 \text{ }^\circ\text{C}$ and $700 \text{ }^\circ\text{C}$. They reported the crystallinity, electrical conductivity and optical absorption of the prepared nanocrystalline cobalt oxide thin films.

2.6. SCOPE OF THE PRESENT INVESTIGATION

Semiconductor based photo electrochemical (PEC) cells offer a simple and efficient means of converting light into dc electricity and can compete with the photovoltaic (e.g. p-n junction and silicon) solar cells. The advantages of PEC cells over that of the conventional photovoltaic cells are as follows;

(I) When coupled in a suitable manner, it may be possible to develop a 'rechargeable' solar cell and thus store electrical energy inside.

(ii) PEC cells can be used in "photoelectrolysis" mode where solar energy can be converted into chemical energy and thus store energy in the form of fuels.

Semiconductors have been used either as single crystal or in the polycrystalline form, and measurements can be made on single crystals increase the reliability. But preparations of single crystals are costly. The polycrystalline materials yield efficiencies close to that of single crystal values and their studies and measurements will continue to be widely pursued research objectives. In recent years, considerable attention has been devoted to the development of low cost solar energy converting device through photoelectrochemical cells. In this regard, polycrystalline photo electrodes of different semiconducting materials have been prepared using different methods, such as electrodeposition, chemical vapour deposition, physical vapour deposition, radio frequency sputtering, magnetron sputtering, spin coating, spray pyrolysis, sol-gel, vacuum evaporation, glow discharge decomposition ion-exchange reactions, electrophoresis, electroless deposition, solution growth pulse plating technique and screen printing etc. have been used to prepare polycrystalline thin film electrodes. However, the quality and the cost of production are more important in practical applications.

In the present investigation, a simple chemical deposition method was adopted to deposit transition metal oxides such as zinc oxide (ZnO), cuprous oxide (Cu_2O), tin oxide (SnO_2) and cobalt oxide (Co_3O_4) on microscopic glass substrates. Various parameters such as substrate temperature, solution concentration, pH of the bath solution will be optimized by trial and error method to obtain device quality

metal oxide thin films of device quality. The obtained metal oxide thin films were being characterized as follows;

- (1) The structural properties of metal oxide thin films studied by X-ray diffraction analysis and FTIR analysis.
- (2) The surface morphology of the thin films analyzed by scanning electron microscopy studies.
- (3) The thickness of the metal oxide thin films measured by weight gain method using the standard formula.
- (4) The nature of the prepared thin film semiconductors evaluated by hot probe method.
- (5) The electrical resistivity of the prepared thin films measured by four probe resistivity meter.
- (6) The optical properties of thin films studied in UV-Visible spectrophotometer to determine their optical band gap values.

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