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Structural and Optical Properties of Zinc - Cobalt Oxide Thin Films Prepared by Chemical Spray Pyrolysis Method: The Effect of Aqueous Solution Molarity

A Thesis

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By

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1.1 General Introduction

An important branch of physics that has been developed in the last decades is the physics of thin films. Thin solid films were probably first obtained by electrolysis in 1838. The term "Thin Films" is used to describe a layer or several layers of atoms of a certain substance whose thickness ranges between (10nm) and less than 1μm (1000nm) [1]. Thin films technique is one of the most recent fully grown technologies that greatly contribute to develop the study of semiconductors and metals by giving a clear indication of their chemical and physical properties. The properties of thin films are usually different from those of the bulk because of the two dimensions nature of thin films. In bulk “three dimensions” the particles are under the influence of forces at all directions, while in thin films the forces act upon the particles at the surface only [2].

Thin films are first made by (Busen & Grove) in 1852 by using (Chemical Reaction) and later in 1857; the scientist (Farady) had been able to obtain a thin metal film by means of (Thermal Evaporation) [3]. Spray pyrolysis was first used commercially more than half a century ago in 1947 as in U.S. patents registered for (H.A.McMaster and W.O.Lytle) to deposited conductive oxide films on heated glass substrate [4]. The film layer is deposited on certain plates chosen according to the nature of the study or the scientific need. Such plates could be glass slides, silicon wafers, aluminum, quartz and others [1]. There are already so many applications of thin films such as the electronic and optical applications.

1.2 Applications of Thin Films

There are already so many applications of thin films. The following are some of the optical and electronic applications:[2, 5, 6] . Thin films are widely used in optical industries, such as mirrors for high reflectance. Also semitransparent reflection coating are used in a number of optical devices such as filters in solar cells, photocells, detectors, and non-absorbing materials are used for interference phenomena. The applications of thin films in electronics have been growing steadily in importance during the last decades. Thin films are widely used in the electronic resistances, capacitances, transistors, integral circuits for digital computers and other electronic equipment's.

1.3 Methods of Preparing Thin Films

The methods of preparing thin film can be divided essentially into two main groups namely physical and chemical methods [6]. These methods are shown in figure (1.1).

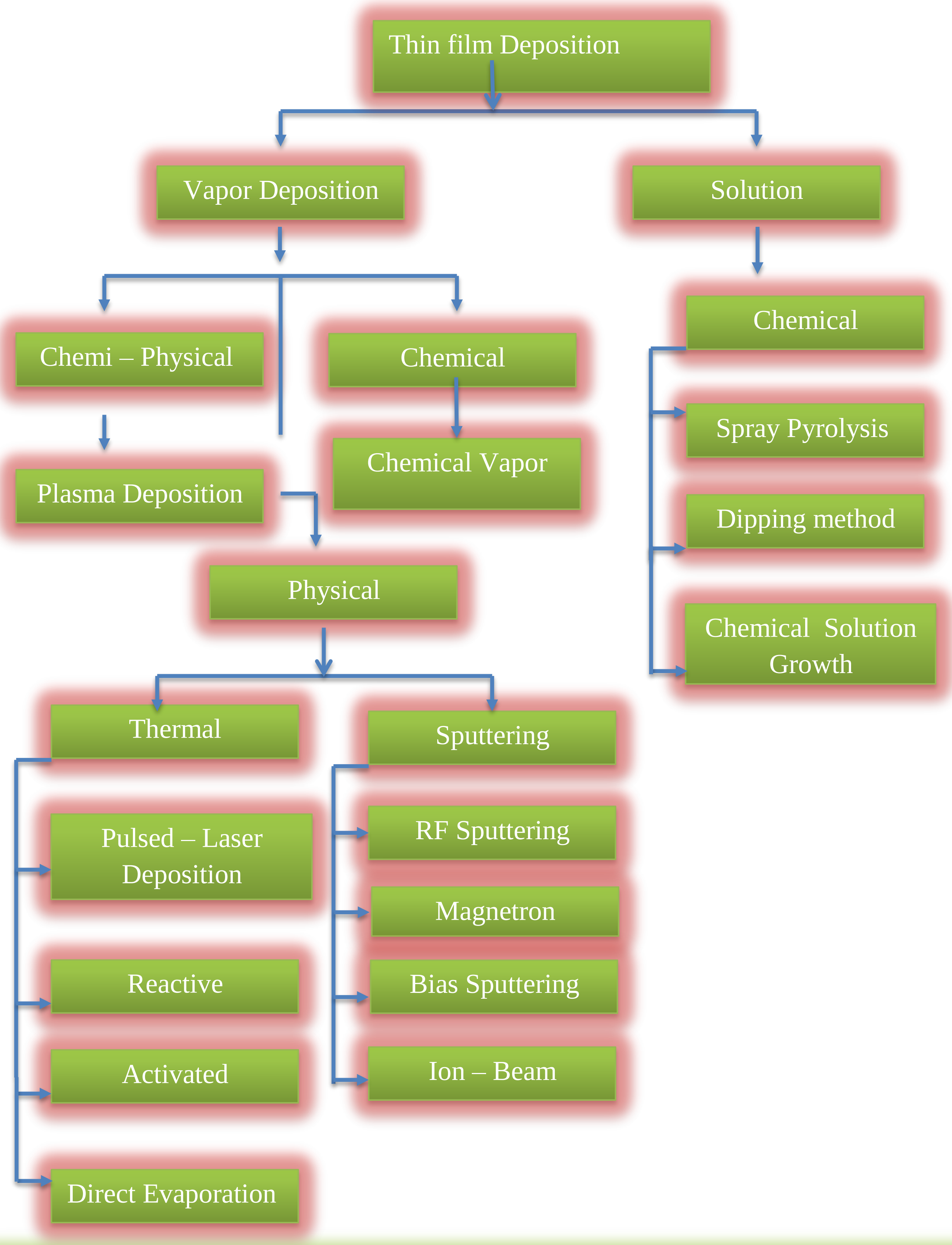

Figure (1.1): Deposition Techniques of thin film deposition techniques [7]

1.3.1 Chemical Spray Pyrolysis Technique

Numerous materials have been prepared in the form of thin film because of their potential technical value and scientific curiosity in their properties. A number of techniques have been examined in the search for the most reliable and cheapest method of producing thin films [8]. Chemical spray pyrolysis (CSP) technique was initially suggested by Chamberlin and Skarman in 1966 to prepare CdS thin films on glass substrates. This method was used by many workers [9,10,11]. Doped and mixed films can be prepared very easily, simply by adding to the spray solution a soluble salt of the desired dopants or impurity. Spray pyrolysis involves spraying of an aqueous solution containing soluble salts of the constituent atoms of the desired compounds to the heated substrates. The liquid droplets vaporize before reaching the substrate or react on it after splashing [12].

1.3.2 Advantages of chemical spray pyrolysis technique

Chemical spray pyrolysis technique has a number of advantages as depicted in the following points [8,13]:

1 . It offers an extremely easy way to dope films with virtually any element in any proportion by merely adding it in some form to the spray solution.

2 . Unlike closed vapor deposition method CSP does not require high quality targets and/or substrates, nor does it require vacuum at any stage which is a great advantage if the technique is to be scaled up for industrial applications .

3 .The deposition rate and the thickness of the film can be easily controlled over a wide range by changing the spray parameters, thus

eliminating the major drawbacks of chemical methods such as sol-gel which produces films of limited thickness.

4 **.** Operating at moderate temperatures (100 – 500 ^0C), CSP can produce films on less robust material.

5 **.** Unlike high – power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local over – heating that can be detrimental for materials to be deposited.

6 **.** By changing composition of the spray solution during the spray process, it can be used to make layered film and films having composition gradients throughout the thickness.

7 **.** It is believed that reliable fundamental kinetic data are more likely to be obtained on particularly well characterized film surface, provided the film are quiet compact, uniform and that no side effects from the substrate occur. CSP offers such an opportunity.

8. Low cost comparing with other methods which require complex devices and instruments with high cost.

1.4 Mechanism of Thin Films Formation

Films growth may be divided into certain stages as shown in figure (1.2). These stages are as follows [14]:

1. Nucleation, during which small nuclei are formed that are statistically distributed (with some exceptions) over the substrate surface.
2. Growth of the nuclei and formation of larger islands, which often have the shape of small (crystallites).
3. Coalescence of the islands (crystallites) and formation of a more or less connected network containing empty channels.
4. Filling of the channels.

It is important to mention that after a certain concentration of nuclei is reached; additional particles do not form further nuclei but adhere to the existing ones
or to the islands formed already.

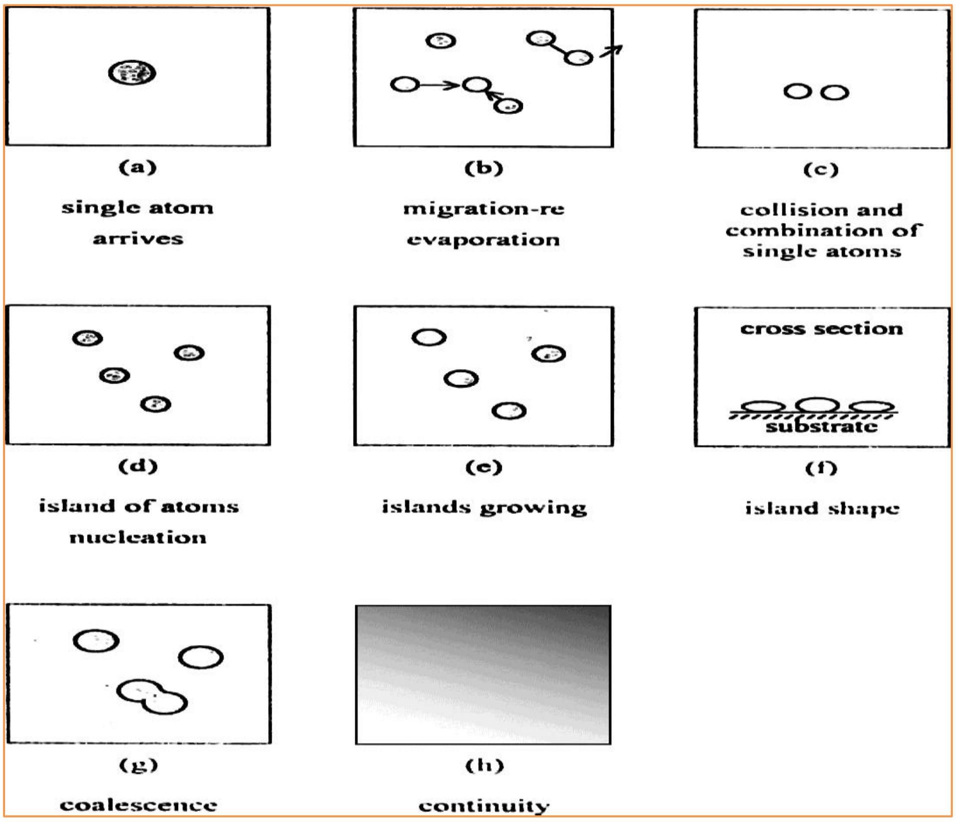

Figure (1.2): Formation Stages of Thin Film [14]

1.5 Transparent Conducting Oxides (TCO)

Transparent Conducting Oxides (TCO) film is a material that is highly transparent in the range of visible light, and at the same time, electrically conductive [15]. The first semitransparent and electrically conductive films were reported as early as 1907. However substantial technological advances were only made after the 1940s when interest on these materials was generated by their potential applications in industry [16]. This material has been used in a wide range of applications in science and technology , including solar cells , heat reflecting mirrors , antireflection coating and a variety of electro-optical devices such as flat panel display devices and many other different applications depending on the type of material; the most popular are ZnO , CdO , In_2O_3 and SnO_2 [17,18]. If these semiconductors are prepared intrinsically i.e. without intrinsic or extrinsic dopants, their resistivity is very high (of the order of $\geq 10^7$ Ω cm). The low resistivity that is required for their application as TCOs can be achieved in two ways:

♦ Creation of intrinsic dopants by lattice defects. These can be oxygen vacancies or metal atoms on respective lattice sites.

♦ Introduction of extrinsic dopants (atoms of foreign materials to the pure form of the original compound). These can be either metals with one additional conduction electron on original metal sites or halogens with one additional electron on oxygen lattice sites [16]. For many application of TCO films the aim is to achieve stable film properties for large area coating processes with low film resistance and high transmittance within the visible spectrum range, by adding oxygen or nitrogen gas into the coating chamber, it is possible to produce oxide or nitride dielectric layers from metal targets [15]. The high optical transparency of these oxides in the visible and near-IR regions of the solar spectrum is a direct consequence of being wide band gap semiconductor ($E_g \geq 3.0$ eV) [19]. Their fundamental absorption edge generally lies in the UV and shifts to shorter wavelengths with increasing carrier concentration. This shift is due to the filling of the states near the bottom of the conduction band and is well known as the Moss-Burstein shift.

1.6 Applications of Thin film Transparent Conducting Oxides (TCO)

The most important applications of transparent conductor Oxides thin films are[20,18,22]:

Solar Cells., Opto- Electronic Devices., Thin film resistors., Gas sensors., Surface acoustic devices, Transparent electrodes, thermal mirrors .

There are wide uses for the TCO for example in ship coating to resist ice and cloud and to remove the electronic charges that settle on glass windows in different device beside their uses as transparent heating metals on the planes and car windows.

1.7 Properties of Zinc oxide

ZnO is one of the most important TCO materials; it is an intrinsic n-type semiconductor which was regarded as one of the important transparent conducting oxide (TCO) with an energy band gap of (3.4eV), is of great use owing to its significant technology applications such as photo-catalysts, solar cells, transparent conductive films and chemical sensors . ZnO can be n-type, easily doped but is difficult to doped p-type [23]. The electrical conductivity of ZnO thin films increases with increasing temperatures as a result of the semiconductor material nature [24] . ZnO has attracted attention as a transparent conducting oxide (TCO) film because of the following features [25]:

Wide band gap (3.37eV), High conductivity, Ease in doping, Chemical stability in hydrogen plasma, Thermal stability when doped with group III elements, Abundance in nature and non-toxicity, Low cost, relatively low deposition temperature, and environmental friendliness, High excitation binding energy.

The important characteristics of the zinc oxide can be summarized in table (1.1) .

Table (1-1) properties of ZnO[25].

Lattice constants a_o , c_o	0.32469 nm , 0.52069 nm
Density	5.606 g / cm^3
Melting point	2248 K
Relative dielectric constant	8.66
Energy gap	3.4 eV (direct)
Exiton binding energy	60 meV
Electron mobility	200 cm^2/V.S
Hole mobility	5 – 50 cm^2 / V.S
Sublimation point	1975 ±25
Optical transparency	0.4 – 2.5 µm
Refractive index	n_o=1.9985 , n_e=2.0147 (λ=632.8nm)
Thermal Conductivity	100 mW/cm K at 300K

ZnO have a large excitation binding of 60 meV at room temperature, it's like GaN, will be important for blue and ultra-violet optical devices. ZnO has several advantages over GaN in this application range however, the most important being its larger exaction binding energy and the ability to grow single crystal substrates. Other favorable aspects of ZnO include its broad chemistry leading to many opportunities for wet chemical etching, low power threshold for optical pumping, radiation hardness and biocompatibility. Together, these properties of ZnO make it an ideal candidate for a variety of devices ranging from sensors through to ultra-violet laser diodes and nanotechnology-based devices such as displays[26].

Most of the II–VI binary compound group semiconductors crystallize in either cubic zinc blende or hexagonal wurtzite structure where each anion is surrounded by four captions at the corners of a tetrahedron, and vice versa, this tetrahedral coordination is typical of sp3 covalent bonding nature, but these materials also have a substantial ionic character that tends to increase the band gap beyond the one expected from the covalent bonding. ZnO is a II–VI compound semiconductor whose iconicity resides at the borderline between the covalent and ionic semiconductors[25].The crystal structures shared by ZnO are wurtzite , zinc blend , and rock salt (or Rochelle salt) as schematically shown in figure (1.3).

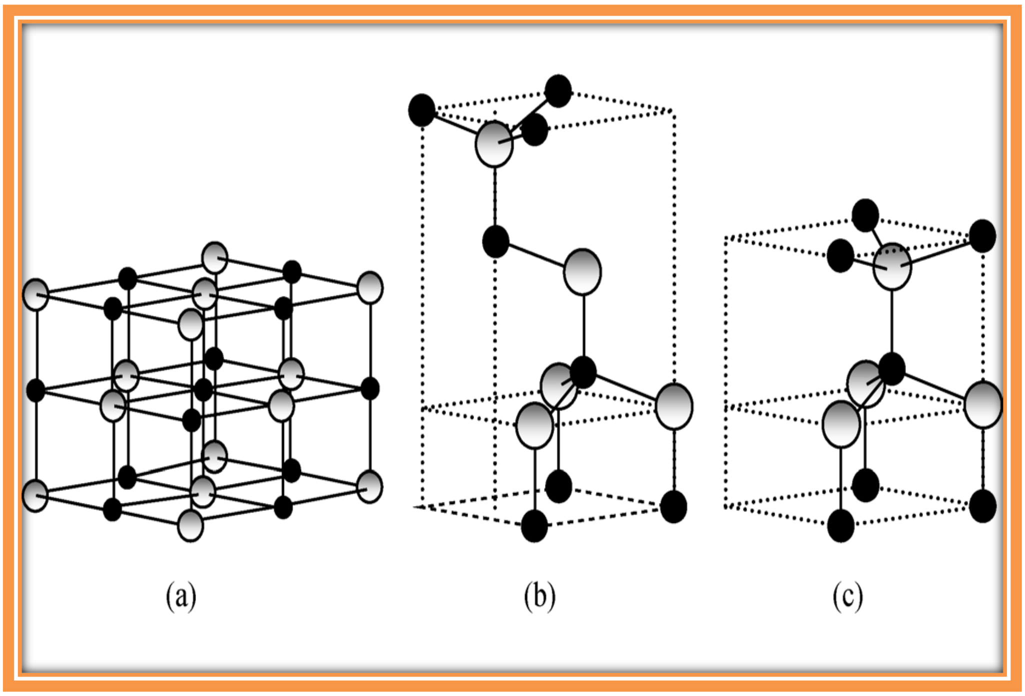

Figure (1.3): Stick-and-ball representation of ZnO crystal structures:(a) cubic rock salt , (b) cubic zinc blend , and (c) hexagonal wurtzite . Shaded grey and black spheres denote Zn and O atoms, respectively.[25]

1.8 Physical and Chemical Properties of The Cobalt Oxide

Cobalt oxide is considered as a p-type semiconductor material. Although there are three different forms of cobalt oxides namely cobaltous oxide (CoO), cobaltic oxide (Co_2O_3) and cobaltite oxide (Co_2O_4), cobaltite oxide is the most widely used in electrochemical capacitor applications. The black tricobalt tetraoxide, Co_2O_4 is usually a product of thermal treatment of cobalt hydroxide, $Co(OH)_2$ at temperatures above 300^oC. Cobalt oxide is also a promising material in gas sensing and solar energy absorption as well as lithium ion battery electrodes. (CoO) has a density of (6.45 g/cm^3) and molecular weight of (74.9326 g/mol). Its melting point is (1933 ^oC) [27] .

1.9 Literature Survey

In 2000, B.J.Lokhand and Uplane L. Uplane [28] studied, thin films of Zinc oxide (ZnO) which were prepared on glass substrates by spray pyrolysis techniques using 0.025 M aqueous solution of Zinc acetate. X-ray diffraction revealed that the films were polycrystalline in nature having hexagonal wurtzite type crystal structure. Estimated band gap energy from optical absorption data was around 3.27 eV.

In 2002, H. Mondragon-Suarez et al. [29] studied Aluminum-doped zinc oxide thin films ZnO:Al deposited on soda-lime glass substrates by the chemical spray technique. The effect of the Al concentration and the type of solvent (methanol, ethanol and isopropanol) in the starting solution, on the resistivity, structure, surface morphology and optical transmittance of the ZnO:Al thin films were studied. All the films were polycrystalline and their surface morphology changed with the type of solvent employed. The optical transmittance was higher than 85% at 550nm. An increase in the Al concentration produced a shift in the absorption edge to higher energies.

In 2003, R. Ayouchi et al. [30] studied structural, morphological, optical and electrical properties of ZnO thin films prepared by chemical spray pyrolysis, on polished Si(100) , and fused silica substrates. Optical properties, have been studied in terms of deposition time and substrate temperature. Growth rate higher than (15nm /min) could be achieved at Ts = 543 K. All the prepared films at substrate temperatures above 473K were polycrystalline with the hexagonal wurtzite structure. The optical band gap of the films decreased from 3.33 to 3.31 eV with the increase at the substrate temperature from (473 to 573 K). The ZnO films prepared in the conditions of the maximum growth rate, present high electrical resistivity, a direct optical band gap (3.31) eV, and optical transmittance of 90% and an antireflective characteristic similar to the TiO_2 thin film in commercial solar cells.

In 2004, Hwang et al. [31] a series of $Zn_{1-x}Mg_xO$ films with various deposition temperatures were prepared on sapphire substrate by magnetron co-sputtering. It was found that the Mg content in the $Zn_{1-x}Mg_xO$ film depended on the deposition temperature. Through transmittance measurements, it was observed that the shift of the absorption edge depended on the deposition temperature due to the difference of surface diffusion of the deposited atoms. From the XRD results, it was observed that all the films exhibited the only (002) peaks indicating the single - phase $Zn_{1-x}Mg_xO$ without changing wurtzite structure of ZnO. These results imply that $Zn_{1-x}Mg_xO$ can be a useful material in synthesizing the lattice matched ZnO-based hetero structure. The crystalline quality and surface morphology of the $Zn_{1-x}Mg_xO$ films also depended on the deposition temperature. Therefore, it is concluded that the deposition temperature is a very important variable in controlling the properties of $Zn_{1-x}Mg_xO$ films.

In 2005, Zhang et al. [32] had prepared $Zn_{1-x}Mg_xO$ films using ultrasonic spray pyrolysis method and found that the band gap of ZnO could be widen with increasing Mg-content. With increasing Mg content, the optical band gap and photoluminescence peak could be tuned to the wider energy while maintaining high crystallinity and without inducing significant change of the lattice constants. The results imply that $Zn_{1-x}Mg_xO$ films can be considered as active layers for band gap engineering such as $Zn_{1-x}Mg_xO$ -based super lattices or quantum wells.

In 2006, Ashour et al. [33], had fabricated ZnO thin films with reasonable structural, electrical and optical properties via a spray pyrolysis technique from water/methanol solution of zinc acetate. It was found from X-ray analysis that the ZnO films are polycrystalline The average crystallite size is around 20 nm. The optical investigations based on the spectrophotometric characteristics have confirmed that the ZnO films sprayed on glass show a high transparency. The deduced absorption index was decreased sharply as the wavelength increased. The films exhibited a direct transition in the range (3.21 - 3.31) eV.

In 2006 , Caglar et al. [34] studied the optical constants of the ZnO crystalline thin film deposited onto glass substrates. X-ray analysis showed the crystallographic structure of the film and the size of the crystallites in the film. Optical constants such as refractive index and extinction coefficient, were determined from transmittance spectrum in the ultraviolet-visible-near infrared (UV-VIS-NIR) regions using envelope method. Absorption coefficient, and the thickness of the film were calculated from interference of transmittance spectra. The energy band gap, and the thickness of the films were evaluated as 3.283 eV and 635 nm, respectively.

In 2006 , Gumus et al. [35] studied the structural and optical properties of zinc oxide thin films deposited on a glass substrate by a spray pyrolysis technique at 400 °C using solution of zinc acetate. The X-ray diffraction analysis showed that film was polycrystalline in nature. The grain size was estimated to be (40) nm. Optical measurements showed that the film possesses high transmittance over (90%) in the visible region sharp absorption edge near 380 nm. Optical measurements show that the film possesses high transmittance over 90% in the visible region and sharp absorption edge near 380 nm. The film has a direct band gap with an optical value of (3.27) eV which is close to the previously reported value (3.28 eV) .

In 2006, Park et al. [36] studied the structure and properties of transparent conductive doped ZnO films thin films grown using the PLD technique deposited on quartz glass substrates. The morphology and the surface roughness determined by AFM measurement The roughness was increased with the increase of substrate temperature and in the same time, the grain size on the surface is varied. The band gap of ZnO, AZO and GZO films are (3.23,3.36 and 3.51 eV), respectively. The high-energy shift of theoptical band gap of GZO and AZO films compared to the ZnO films are due to the much higher carrier concentration of these doped films and filling of electronic states of the conduction band (Burstein-Moss-Shift).

In 2007, Luo et al. [37] had deposited $Zn_{1-X}(Mg,Cd)_X O$ films on single crystal Si (100) substrate using ultrasonic spray pyrolysis under ambient atmosphere. The X-ray diffraction patterns confirmed the existence of a ZnO single-phase with a hexagonal wurtzite structure.

In 2007, S. Ilican et al. [38] prepared ZnO thin films by the spray pyrolysis method at ($350\,^{0}C$) on glass substrates. The structural properties were studied by X-ray diffraction measurements. The average dimensions of crystallites were determined by the Scherrer method from the broadening of the diffraction peaks taking into account the instrumental broadening with a hexagonal wurtzite structure of the bulk and lattice constants:(a = 3.24982 Å), (c = 5.20661 Å).

In 2007, Yakuphanoglu et al. [39] investigated the influence of fluorine on the structural, surface morphology and optical properties of ZnO thin films. from X-Ray diffraction results it was found that all films have polycrystalline nature. A ZnO single phase with a hexagonal wurtzite structure was observed in structure of the films. The crystalline size for the films was calculated using a well-known Scherrer's formula and the obtained values were in the range of 27–40 nm. The values of direct band gap were determined and these values change with fluorine (F) content. The shift of absorption edge was associated with Burstein–Moss effect.

In 2008, Chanipat Euvananont et al. [40] studied Aluminum-doped ZnO (ZnO:Al) films prepared by spray pyrolysis using zinc acetate in methanol as a precursor solution and $AlCl_3$ as a dopant. It was found that all films exhibited a preferred crystallographic orientation. The average crystallite sizes calculated from X-ray diffraction data ranged from 19 to 22 nm, while dark-field TEM images exhibited individual crystallites ranging from approximately 10 to 100 nm in size. Scanning electron micrographs revealed porous structures comprising petal-shaped grains, most of which were significantly larger than the calculated crystallite sizes, indicating that such grains comprise multiple crystallites. Any effects of the Al doping concentration on the crystal structure or the microstructure of the ZnO films were not apparent from the results.

In 2008, Bhatti and Malik. [41] studied Aluminum-doped ZnO (ZnO:Al) films prepared by spray pyrolysis using Zinc acetate dehydrate [$Zn(CH_3COO)_2$_$2H_2O$] and cobalt acetate tetrahydrate [$Co(CH_3COO)_2$_$4H_2O$] as precursors and their powders in the desired molar ratio were dissolved in methanol onto quartz and glass substrates. At the optimum temperature of $380\,^{0}C$ X-Ray diffraction results revealed the films have an Wurtzite structure. In addition, the films were found to be textured along [100]. The films having different Co concentration have almost similar surface morphology and microstructure.

In 2008, Ilican et al. [42] prepared and characterized ZnO thin films deposited by the sol-gel spin coating method on glass substrates using Zinc acetate dehydrate. The crystal structure and orientation of the ZnO thin films were investigated by X-ray diffraction (XRD) patterns. FWHM of thin films shows an increase with increasing chuck rotation rate. The grain size of crystallites was calculated using Scherrer's Formula. It was observed that the grain size values decrease with increasing chuck rotation rate, which clearly reveals the deterioration in the crystallinity. Dislocation densities exhibit an increasing trend with increasing chuck rotation rate, which leads to the increasing in the concentration of lattice imperfections. The optical absorption studies reveal that the transition is direct band gap energy. The optical band gaps and urbach energies of the thin films were determined. The shift of absorption edge is associated with Burstein-Moss effect.

In 2009, Samuel et al. [43] prepared Zinc Oxide nanoparticles by chemical method. The alkali solution of zinc was prepared by dissolving zinc nitrate [Zn $(NO_3)_2 \cdot 6H_2O$] and KOH. The reaction solution was heated to ($50\,^0C$) temperature and keeping the PH 8. The structural and optical properties of the prepared ZnO particles have been confirmed using TEM, XRD and UV-VIS absorption spectroscopy. All of the diffraction pattern could be indexed to the hexagonal ZnO phase (Wurtzite Structure) .

In 2009, Islam and Podder. [44], prepared Zinc Oxide nano fiber thin films deposited on cleaned glass substrate by a simple spray pyrolysis technique under atmospheric pressure using zinc acetate precursor zinc acetate [$Zn(CH_3COO)_2.2H_2O$] at temperature of (200°C). The surface properties of the films were examined by using Scanning Electron Microscope (SEM) . The films show direct band gap in the range (3.3 – 3.4 eV). The films exhibit low absorbance in the visible - near infrared region from ~ 450 nm to 1000 nm. Variations in the optical constants with wavelength were found to be thickness dependent of the films. The optical properties refractive index, optical band gap and low dielectric constant of the as-deposited and annealed films show the suitability of the deposited films for using them in optoelectronic devices and solar cells.

In 2010, Kim et al. [45] studied Ga-doped ZnO (ZnO:Ga) thin films prepared on glass substrate by RF magnetron sputtering method. The optical band gap of thin films showed the lower blue shift than the theoretical value of the Burstein–Moss (BM) effect. The shift of bandgap was dependent on the carrier concentration and acquired by combining the no parabolic BM effect and band gap narrowing (BGN).

In 2010 Ying-Lan et al. [46], investigated of the effects of substrate on the structure, morphology and optical properties of vertically aligned ZnO nanorod arrays by the wet chemical bath deposition (CBD) method. The wet CBD method was employed to fabricate ZnO nanorods with special attention paid to the effects of the substrates on the structure, morphology and optical properties of as-grown ZnO nanorods at a relatively low temperature of ($95^{\circ}C$). X-ray diffraction (XRD) and scanning electron microscope (SEM) results illustrated that the ZnO nanorod arrays with hexagonal wurtzite structure are grown densely and vertically on all the substrates, whereas the average diameter and length were found to be closely related to the substrates nature.

In 2010 Bahadur et al. [47] investigated the Influence of cobalt doping on the crystalline structure, optical and mechanical properties of ZnO thin films by sol–gel spin coating technique. The X-ray diffraction (XRD) patterns of $Zn_{1-x}Co_xO$ showed the standard ZnO diffraction pattern and identified as the wurtzite structure (hexagonal; a=0.33 nm, c=0.52 nm) . Influence of Co addition on the volume fraction of grain boundaries has been interpreted. Increase in Co content in the range $0 \le x \le 0.10$ led to quenching of near-band edge and blue emissions, decrease in band gap energy (Eg) from 3.36 eV to 3.26 eV, decrease in film thickness and refractive index and an increase in extinction coefficient of $Zn_{1-x}Co_xO$ thin films.

In 2010, Murugesan and Achuthanunni [48], studied the structure and optical properties of undpped and Co doped ZnO nanostructured thin films deposited on glass substrates by the sol-gel dip coating method. The XRD patterns of all nano structured films show the crystalline behavior and are of a hexagonal wurtzite structure. The optical studies show that the band gap of ZnO:Co decreases the (d) electron of the Co atom and band carriers of the host material. This unique property of ZnCoO films can be used to fabricate transparent electrodes in flat panel displays and metal-insulator-semiconductor diodes.

In 2010, Erhaima,et al. [49] studied the structural and optical properties of cobalt-doped zinc oxide thin films prepared by spray pyrolysis technique using solution of zinc acetate ($Zn(CH_3COO)_2.2H_2O$) and cobalt chloride ($CoCl_2$) deposited on glass substrates at ($400\,^0C$). It was shown that the the thin films have a polycrystalline texture with a wurtzite hexagonal structure, and the grain size was decreased with increasing Co concentration, and no change was observed in lattice constants while the optical band gap decreased from (3.18-3.02) eV for direct allowed transition. Other parameters such as texture coefficient, dislocation density and number of crystals (N) were also calculated.

In 2010, Supriya et al. [50] have prepared cobalt doped zinc oxide $Zn_{(1-x)}Co_xO$ films grown by spray pyrolysis technique at different substrate temperatures in the range, 260- 350°C on ultrasonically cleaned glass substrates using zinc acetate, $Zn\ (CH_3COO)_2.\ 2H_2O$ and cobalt acetate, $Co\ (CH_3COO)_2.4H_2O$ The X-ray diffraction studies revealed that all the layers exhibited wurtzite structure with (002) plane as the preferred orientation. The grain size of the films was varied in the range, (20 - 40 nm). The average optical transmittance of the films was found to be > 75% in the visible region and the evaluated optical band gap of the films decreased from 3.37eV to 3.22 eV with the increase of substrate temperature.

In 2011, Tewari and Bhattacharjee [51] deposited ZnO thin film on cleaned glass substrates by chemical spray pyrolysis technique using

$Zn(CH_3COO)_2$ as precursor solution .Also, aluminum-doped ZnO thin films were prepared by using $AlCl_3$ as doping solution for aluminum. The dopant concentration [Al/Zn atomic percentage (at%)] was varied from 0 to 1.5 at% in thin films of ZnO prepared in different depositions. It was confirmed that all the films were of zinc oxide having polycrystalline nature and possessing typical hexagonal wurtzite structure with crystallite size varying between 100.7 and 268.6 nm. The films exhibited changes in relative intensities and crystallite size with changes in the doping concentration of Al. The films exhibited distinct changes in their optical properties at different doping concentrations, including a blue shift and slight widening of band gap with increasing Al dopant concentration.

In 2011, Sarsari et al. [52] studied the optical, structural, and magnetic properties of ZnO:Co nanoparticles prepared by a thermal treatment of ball milled precursors using zinc acetate dehydrates (Zn $(CH_3COO)_2 \cdot 2H_2O$), cobalt acetate tetra hydrate ($Co(CH_3COO)_2 \cdot 4H_2O$) The XRD results showed that a very low concentration of cobalt has little effect on the lattice parameters and same strain for all samples. The UV-vis absorption of the samples showed that the band gap of samples decreased from (3.27eV to 3.17 eV) by increasing cobalt concentration from (0.02 to 0.08).

In 2012, Udayakumaret et al. [53] cobalt doped zinc oxide nanoparticles were prepared through simple chemical precipitation method at room temperature. The average grain size of the pure (ZnO: Co) samples were calculated from the full width half maximum (FWHM) of the diffraction peaks using the Debye–Scherrer equation and the absorption band between (338-341.4) originates from ZnO. The position of the absorption spectra is observed to shift towards the lower wavelength side with increasing Co doping concentration in ZnO. This indicates that the band gap of ZnO material increase with doping concentration of Co^{2+} ions. The increase in the band gap (or) blue shift could be explained by the Burstein–effect. This is the phenomenon that the Fermi level merges into the conduction band with the increase of the carrier concentration.

In 2012, Prajapati and Sahay [54] studied alcohol-sensing characteristics of spray deposited ZnO nanoparticle thin films deposited on cleaned glass substrates by spray pyrolysis. XRD analyses confirmed that the films were polycrystalline zinc oxide, possessing hexagonal wurtzite structure with crystallite size(25) nm. The SEM micrograph of the film showed a good uniformity and a dense surface having spherical-shaped grains. Alcohol sensing characteristics of the deposited films had been investigated for various concentrations of methanol, ethanol and propanol in air at different operating temperatures.

In 2013 Nath et al. [55] studied the structural and optical characterization of cobalt-doped ZnO thin films deposited on glass substrates by spray pyrolysis method at a relatively lower temperature of (230°C). The XRD patterns peaks at confirmed the hexagonal wurtzite structure of the samples. In this study. The optical transmittance increases in the visible region and decreases in the ultraviolet region for all the samples. But in the visible region with the increase of (0-7%) Co^{2+} concentration, there is a gradual decrease in the transmittance spectra of the samples. The optical energy gaps of the Co-doped ZnO samples are considerably smaller, showing thereby that the band gap of ZnO can be tuned by Co-doping. All co-doped samples gave UV as well as blue-green emissions, somewhat weaker than in undoped ZnO.

In (2013),Ashok kumar et al. [56] studied the deposition of polycrystalline ZnO thin films on glass substrate by spray pyrolysis technique at (250°C) using aqueous solution of zinc acetate. From the transmission spectrum within the region of UV-VIS-NIR, the optical constant such as refractive index and extinction coefficient were determined. The films were found to exhibit a low absorbance and reflectance and high transmittance in the visible region. The thickness of the film was calculated using the gravimetric method and band energy gap of thin films were evaluated as (1.9 µm and 3.2 eV) respectively. The atomic force microscopy (AFM) image was used to analyze the morphological structure of ZnO film. The X-Ray diffraction study revealed that the developed films were polycrystalline.

In 2014 Jabbar and Ali [57], studied the structural properties of boron and aluminum co-doped zinc oxide nanostructure films deposited at 450 ^{0}C on glass substrates by chemical spray pyrolysis in (150±5 nm). The structure of AZB nano structure films had been found to exhibit the hexagonal wurtzite structure. The increase of AZB concentration caused to decrease the crystallite size. The structural details and micro structure were obtained from X-ray diffraction, atomic force microscope (AFM) and scanning electron microscope(SEM).

In 2014, Ali [58], investigated the molarities effect on structural and optical properties of ZnO prepared by spray pyrolysis with different molarities (0.05 , 0.1 , 0.15 , and 0.2). The studies were focused on the effect of variation of aqueous solution molarity on the ZnO thin films.

Increasing of solution molarity caused the decrease in the smoothing and homogeneity of the films and shape factor , further it exhibited increase in intensity of the peak preferred orientation (002) plane (from about 1700 to 4000) , integral breadth (from 0.015 to 0.016) deg. Decreased transmission especially in the NIR region at 800 nm (from 90% to 55%) and band gap (from 3.12 to 3.02) eV. It was concluded that the films were more suitable for acoustic applications, due to the scattering effect recorded.

1.10 Objectives of the study

The main objectives of this work are :

1.Preparation of $Zn_{1-x}Co_xO$ thin films where X= (0,0.02,0.15,0.2) on glass substrate with different Co-molarity by spray pyrolysis (CSP) technique at substrate temperature of (400 ±5 ^oC).

2.Studying the effect of aqueous solution molarity and cobalt concentration on the surface morphology, structural and optical properties of the deposited thin films.