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Synthesis and Characterization of Some Metal Oxides Nanostructure Thin Films for Gas Sensor Application

A Thesis

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of Diyala in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy of Science in Physics*

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنْتَ

الْعَلِيمُ الْحَكِيمُ

صدق الله العظيم

سورة البقرة

الاية ٣٢

Dedication

My PhD is dedicated to...

*My father and mother soul, who were my
endless support along my life until I reached to
this stage.*

My lovely wife.

My supporters brothers and sister.

*My beautiful children.....Zhwar, Zhiya and
Sharyia.*

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List of Symbols

<i>Symbol</i>	<i>Definition</i>
\AA	Angstrom
θ	Diffraction Angle
t	Thickness
hkl	Miller Indices
k_B	Boltzmann's Constant
$h\nu$	Photon Energy
α	Absorption Coefficient
A' and B	Constants Depending on Properties of Conduction and Valance Bands
ν	Frequency
d	Inter planar spacing
λ	Wavelength
n_0	Number of Grains Per Unit Area
δ	Dislocation Density
E_g	Energy Band Gap
E_v	Valence Band Energy
E_c	Conduction Band Energy
h	Planck's Constant
J	Current Density
T	Transmittance
μ	The Mobility
μ_n	Mobility of Electron
μ_p	Mobility of Hole
τ	Carrier's Lifetime
v_d	Drift Velocity
m^*	Effective Mass

σ	Electrical Conductivity
σ_o	Minimum Electrical Conductivity
E_a	Activation Energy
B	Magnetic Field
R_H	Hall Coefficient
V_H	Hall Voltage
μ_H	Hall Mobility
V_{bi}	Built - In Voltage
q or e	Electron Charge

List of Abbreviations

<i>Abbreviations</i>	<i>Definition</i>
APCVD	Atmospheric Pressure Chemical Vapor Deposition
CVD	Chemical Vapor Deposition
XRD	X-Ray Diffraction
FE-SEM	Field Emission Scanning Electron Microscopy
AFM	Atomic Force Microscopy
UV Vis.	Ultraviolet Visible
EDS	Energy Dispersive Spectroscopy
FWHM	Full Width at Half Maximum
PVD	Physical Vapor Deposition
<i>ppm</i>	Part Per Million
NPs	Nanoparticles
ICSD	Inorganic Crystal Structure Database
<i>PLAL</i>	Pulse Laser Ablation in Liquid
MOCVD	Metal Organic Chemical Vapor Deposition
GIXRD	Grazing Incidence X-Ray Diffraction
D.C	Direct Current
A.C	Alternating Current
PC	Photoconductivity
I-V	Current-Voltage
RT	Room-Temperature
C.B	Conduction Band
V.B	Valance Band
NCs	Nanocomposites
W-H	Williamson-Hall
NSTF	Nanostructured thin film
HMTA	Hexamethylenetetramine
NRs	Nanorods

Abstract

In this work, metal oxide (SnO_2 and ZnO) nanostructures thin films were deposited on the glass substrate by atmospheric pressure chemical vapor deposition (APCVD) and hydrothermal drop casting techniques.

The main materials, which are used in this process, are tin chloride, zinc acetate, zinc nitrate and hexamethylenetetramine (HMTA). The first study involved the use of the APCVD system to obtain the optimized thin films by taking appropriate deposition conditions, such as flow rate of gas inside the system, substrate temperature, quality and location of deposition within the system reactor. The structural, morphology, surface roughness and optical properties are studied by x-ray diffraction (XRD). Field emission scanning electron microscopy (FE-SEM), Energy Dispersive X-ray Spectroscopy (EDS), atomic force microscope (AFM), UV-Vis. spectroscopy respectively and gas sensing properties have been investigated for (SnO_2 and ZnO) thin films. X-ray diffraction (XRD) analyses taken for all samples were prepared by different oxygen gas flow rates (4, 5, 6, and 8NL/h) and different substrate temperatures (300, 400, 450, 500, 550 and 600°C). It was observed that by increasing the oxygen flow rates and substrate temperatures, the crystallite size increased. The XRD results showed that the SnO_2 nanostructure thin films are polycrystalline in nature with a tetragonal structure, while ZnO has a hexagonal structure. The crystallite size was estimated by Scherrer formula and W-H analyses. Also, it was noted that the dominant in an orientation corresponds to [100] due to increasing the annealing temperatures (150, 200, 250, and 300 °C) which were prepared by hydrothermal drop casting. (FE-SEM) image manifested the surface morphology of the (SnO_2 and ZnO) deposited on a glass substrate. Clearly, it was found that the sample of nanostructure thin films deposited with a gas flow rate of (4NL/h) at substrate temperature 400°C has the

smallest grain size. However, the result revealed that through increasing the gas flow rate and substrate temperature, the grain size increased as well. The FE-SEM images of SnO₂ nanostructure thin films clearly indicate that the shapes of balls or cubes are shown in their structures, while the ZnO thin films have a cauliflower-like or sponge, nanorod and nanoflower shapes. EDX analysis showed accurately the growth of (SnO₂ and ZnO) on the glass substrate and the purity of these thin films with the ratio of the material drift on the surface of the substrates. Atomic Force Microscopy (AFM) appeared that the grain size becomes larger, the crystallinity was improved with an increase in the substrate temperature, and the distribution of grains is uniform on the substrate surface. The optical properties evinced the energy gap for the direct allowed electronic transition which was calculated using Tauc's equation. It is noticed that SnO₂ thin films fall in the range of (3.72- 4.09eV), and ZnO thin films in the range of (3.18-3.48 eV), depending upon the oxygen gas flow rate, deposition time and substrate temperatures. The electrical properties include Resistance–Temperature Characteristic, D.C. electric conductivity, and Hall effect measurements. Activation energies and electrical conductivity (σ_{RT}) were measured for SnO₂ nanostructure thin films. The results of Hall coefficient showed that the SnO₂ nanostructure thin films follow the n-type semiconductor behavior. Gas sensor test was done at room temperature for (100 ppm) ethanol gas exposed to SnO₂ thin films that prepared at (400, 450 and 500°C) substrates temperatures, and indicated that the sensitivity of the samples decreases with increase the substrate temperature due to the morphology surfaces and particle size of the films. In other words, the sensitivity of the sensor increases with decreasing the particle size of the SnO₂ nanostructure thin film. The response and recovery time increase with an increase in the ethanol gas concentration ranged from (100- 1000 ppm). A fast response speed at (7s)

was noted with recovery time (14s) at (100 ppm), while the slow response speed was observed for (1000 ppm) at (8.7s) with a recovery time of (16 s).

1.1 Introduction

Metal oxides are compounds composed of metal atoms and oxygen. There are many metals exist in nature as native metal oxide ores. Aluminum oxide is a widely abundant example accounting for 8.1% of the earth's crust. The high natural abundance of metal oxides is due to the formation of stable chemical bonds between the electronegative oxygen atoms and the metal. The majority of metals can readily oxidize to metal oxide materials in the presence of oxygen, for example chromium oxidized in air readily forming a protective metal oxide layer. The rate of oxidation can be enhanced by the presence of water, as exhibited by iron which oxidizes much more easily in hydrated environments. This enhanced rate of oxidation can be referred to the formation of hydroxyl groups on the surface. Metal oxides tend to adopt mostly ionic structures with metal-oxygen-metal crosslinks which in many instances creates an insoluble material in most solvents. The use and application of metal oxide thin films are long established but still growing in market, particularly in the microelectronics industry, where metal oxides are used as components in capacitors, transistors, computer memories and as semiconducting materials. Metal oxide thin films also have a widespread use as functional coatings for glass, including as self-cleaning glass systems for durability enhancement and as low emissivity coatings for energy efficient glass installations [1]. In this work, the synthesization and characterization of (SnO_2 and ZnO) nanostructure thin films with unique properties have been developed for applications in gas sensing field. The (APCVD) and hydrothermal drop casting have been used as a main route to synthesize thin films. Some metal oxide semiconductors are able to change their conductivity on the basis of adsorption of different types of gases and gas concentrations. These changes can be transformed into electric signals, and this property is today used to create gas detectors

based on oxide semiconductors [2, 3]. However, great interest on metal oxide nanostructures and their applications have been shown by researchers, due to their safe, easy, environmental friendly, cheap synthesis procedure and technological applications in the fabrication of devices for energy harvesting and storage sensors, photonics, as well as medical and biological applications [4]. Semiconducting Metal Oxide (SMO) gas sensors are designed to react with one class of gases, whereby the (SMO) undergoes oxidation or reduction. This process causes the (SMO) sensors to interchange electrons with the target gas at a certain characteristic rate, thereby affecting the sensor's resistance and yielding a certain signal. Through the available gas sensing methods, the gas sensor devices have several unique advantages, such as small size, low cost, ease of fabrication, measurement simplicity, and durability. The principle of operation of metal oxide sensors is based on the change in conductance of the oxide on interaction with a gas, and the change is usually proportional to the concentration of the gas [5, 6]. Generally, there are two types of metal oxide sensors; n-type (zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide), which respond to reducing gases and p-type (nickel oxide, cobalt oxide), which respond to oxidizing gases [7].

1.2 Nanostructured and nanocrystalline

Nanostructured materials are defined as solid materials with at least one characteristic structural length in the order of few nanometers [8]. Nanocrystalline (NC) material is a polycrystalline material with a crystallite size of only few nanometers. These materials fill the gap between the amorphous materials without any long-range order and the conventional coarse-grained materials. Definitions vary, but nanocrystalline material is commonly defined as a crystallite (grain) size below 100 nm. Grain sizes from (100–500 nm) are typically considered

ultrafine grains [9]. The size of nanoparticles distinguishes them from larger crystals, for example, silicon nanocrystals can provide efficient light emission, while bulk silicon does not [10]. The grain size of (NC) sample can be estimated using x-ray diffraction [11]. In materials with very small grain sizes, the diffraction peaks will be broadened. This broadening can be related to a crystallite size using the Scherrer equation [12]. When embedded in solids, nanocrystals may exhibit much more complex melting behavior than conventional solids [13], and may form the basis of a special class of solids [14]. They can behave as single-domain systems (a volume within the system having the same atomic or molecular arrangement throughout) that can help explain the behavior of macroscopic samples of a similar material without the complicating presence of grain boundaries and other defects [15].

1.3 Nanomaterial's

Nanomaterial's describe, in principle, the materials of which a single unit is sized (in at least one dimension) between 1 to 1000 nanometres (10^{-9} m) but usually is 1 to 100 nm (the usual definition of nanoscale) [16]. The nanoscopic scale (or nanoscale) normally refers to structures with a length scale applicable to nanotechnology, usually cited as 1–100 nanometers. A nanometer is a billionth of a meter. The nanomaterial also can be defined as a "material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale". This includes both nano-objects, which are discrete pieces of material, and nanostructured materials, which have internal or surface structure on the nanoscale; a nanomaterial may be a member of both these categories [17]. Nanomaterials and composites can be prepared by different methods. Besides the fabrication of clusters, thin films and coatings from the gas or liquid phase, chemical methods, such as sol–gel

processes, chemical vapor deposition, and hydrothermal deposition are common methods of processing. However, mechanical methods have been developed which allow fabricating nanostructured or nanocrystalline materials in very large quantities with a broad range of chemical compositions and atomic structures and even in bulk shape. With submicron grain sizes in the range of a few hundred nanometers, and other methods such as high pressure torsion straining [18] are inherently limited to small amounts of material, while some methods, such as repeated cold-rolling [19, 20] have been shown to allow the production of bulk quantities of truly nanocrystalline material.

1.4 Tin Oxide

The tin chemistry is made of oxidation number of the metal, with the +2 or +4 oxidation states. Therefore, tin oxide chemistry is dictated by these oxidation states with two main oxides; tin (II) oxide, predominately referred to as stannous oxide, and tin (IV) oxide, or stannic oxide. Intermediate phases of Sn_2O_3 and Sn_3O_4 which contain a mixture of Sn (II) and Sn (IV) oxidation states have also been reported by (A. Kudo and A. Seko) [21, 22]. SnO and SnO_2 have quite different structural and electronic properties, therefore, they give a rise to different applications [23]. Tin oxide (SnO_2) is a stable material. Crystalline tin (IV) is a structural component of tin oxide. This structure has a rutile structure, with six-coordinate tin atoms bound to three-coordinate oxygen atoms. It has a high polarity covalent with the electron-rich oxide character located in the valance and conduction bands [24].

1.4.1 Properties of SnO_2

The (SnO_2), also known as stannic oxide, is an inorganic compound. The mineral form of SnO_2 is called cassiterite, and this is the main ore of tin

[25]. It is a colorless, diamagnetic and solid material. It occurs naturally. Synthetic tin (IV) oxide is produced by burning tin metal in air [26]. Annual production is in the range of 10 kilotons [27, 28]. It is insoluble in water and it can be dissolved in base and acid [29]. Table (1.1) shows some of the properties of tin oxide (SnO_2). Stannic acid indicates to hydrate tin oxide, SnO_2 , which is also called stannic hydroxide [30]. It is used in sensors of combustible gases including carbon monoxide detectors. When the sensor area is heated to a constant temperature and in the presence of a combustible gas, the electrical resistivity drops [30]. Doping with various compounds has been investigated, e.g. with Copper (II) oxide or cupric oxide [31]. Doping with cobalt and manganese gives a material that can be used, in example, high voltage visitors [32]. Tin (IV) oxide can be doped with the oxides of iron [33].

Table 1.1: The properties of SnO_2 [34].

No	Properties	Values
1	Molar mass	150.71 g/mol
2	Appearance	White or light grey powder
3	Density	6.86 g/cm ³
4	Melting point	1630 °C
5	Band gap	(3.6- 4.0 eV), direct
6	Magnetic susceptibility (χ)	-4.1×10^{-5} cm ³ /mol
7	Refractive index	2.006

1.5 Zinc Oxide

Zinc Oxide (ZnO) is an inorganic compound commonly used in the form of white powder soluble in water. It is widely used in industrial products, including glass, plastic, ceramic, medical, pigment, ferrite, etc. Due to its multiple applications in the field of manufacturing electronic devices, it is an important key in the manufacturing of multiple industries [35, 36]. The zinc oxide materials that are resistant to radiation, making it a favorite material in the middle of radiation, especially when the satellite orbits are

close to the earth [37]. It can be used in optical electronics, which include light-emitting diodes, laser diodes, and optical detectors [38]. The zinc oxide thin films are important materials for the manufacture of transistors on a glass substrate as well as in the manufacture of solar cells because they have high permeability in the visible region [39].

1.5.1 Properties of (ZnO)

In materials science, (ZnO) is categorized as a one of the semiconductors belonging to the second and sixth groups in the periodic table, characterized by a relatively large direct band gap up to (3.4 eV), and the excited binding energy is very high nearly about (60 meV) [35]. Table (1.2) shows some of the properties of zinc oxide. It possesses a high permeability in the visible region and a good reflectivity in the near infrared region with a conductivity of negative type (n-type) of semiconductor, these and other characteristics made it possible to use in various applications [40, 41].

Table 1.2: The properties of ZnO [34].

No	Properties	Values
1	Molar mass	81.406 g/mol
2	Appearance	White solid
3	Density	5.6 g/cm ³
4	Melting point	1974 °C
5	Band gap	(3.2- 3.4 eV), direct
6	Magnetic susceptibility (χ)	-27 x 10 ⁻⁶ cm ³ /mol
7	Refractive index	2.029

1.6 Thin Films

A solid material is said to be in a thin film form when it is grown up, as a thin layer on a solid support, called substrate, which can be controlled via the intensification of the individual atomic, molecular, or ionic species, either directly via a physical method, or by a chemical or electrochemical

reactions. Since, the individual atomic, molecular, or ionic species of matter may exist either in the vapor or in the liquid phase. The techniques of thin film deposition can be broadly classified into two main groups: Liquid-phase/solution deposition and vapor phase deposition. It should be emphasized here that it is not simply the small thickness endows thin films with special and distinctive properties, but rather the microstructure resulting from the unique way of their coming into being by the progressive addition of the basic building blocks one by one, which is more important. For thin films, the deviations from the properties of the corresponding bulk materials arise because of their small thickness, large surface-to-volume ratio, and individual physical structure, which is a direct result of the growth processing. Some of the phenomena arising as a natural consequence of small thickness are the optical interference, electronic tunneling through an insulating layer, high resistivity and low-temperature coefficient of resistance. Similarly, the enhancement of the superconducting transition temperature, abrasion resistance, hardness, thermo power and, optical absorption arises in thin films of certain materials having metastable disordered structures [42].

1.7 Classification of Deposition Technique

From the deposition nature, the thin film techniques can be classified into a chemical vapor deposition (CVD) and a physical vapor deposition (PVD) technique. Generally, in the CVD technique the gas/liquid phase of target material undergoes a chemical reaction during the deposition process. In the PVD technique, the deposition is carried out through the vaporization of target materials by either thermal or a thermal process. Where, the target material undergoes sublimation or evaporation through the supply of thermal energy in either thermal. However in a thermal process, the vaporization takes places physically by striking the ionized

gas molecules over the target material. The thin film technique based on the nature of the deposition process can be classified in to physical vapor and chemical vapor deposition [43]. The thin film technique based on the nature of the deposition process can be classification as shown in figure (1.1).

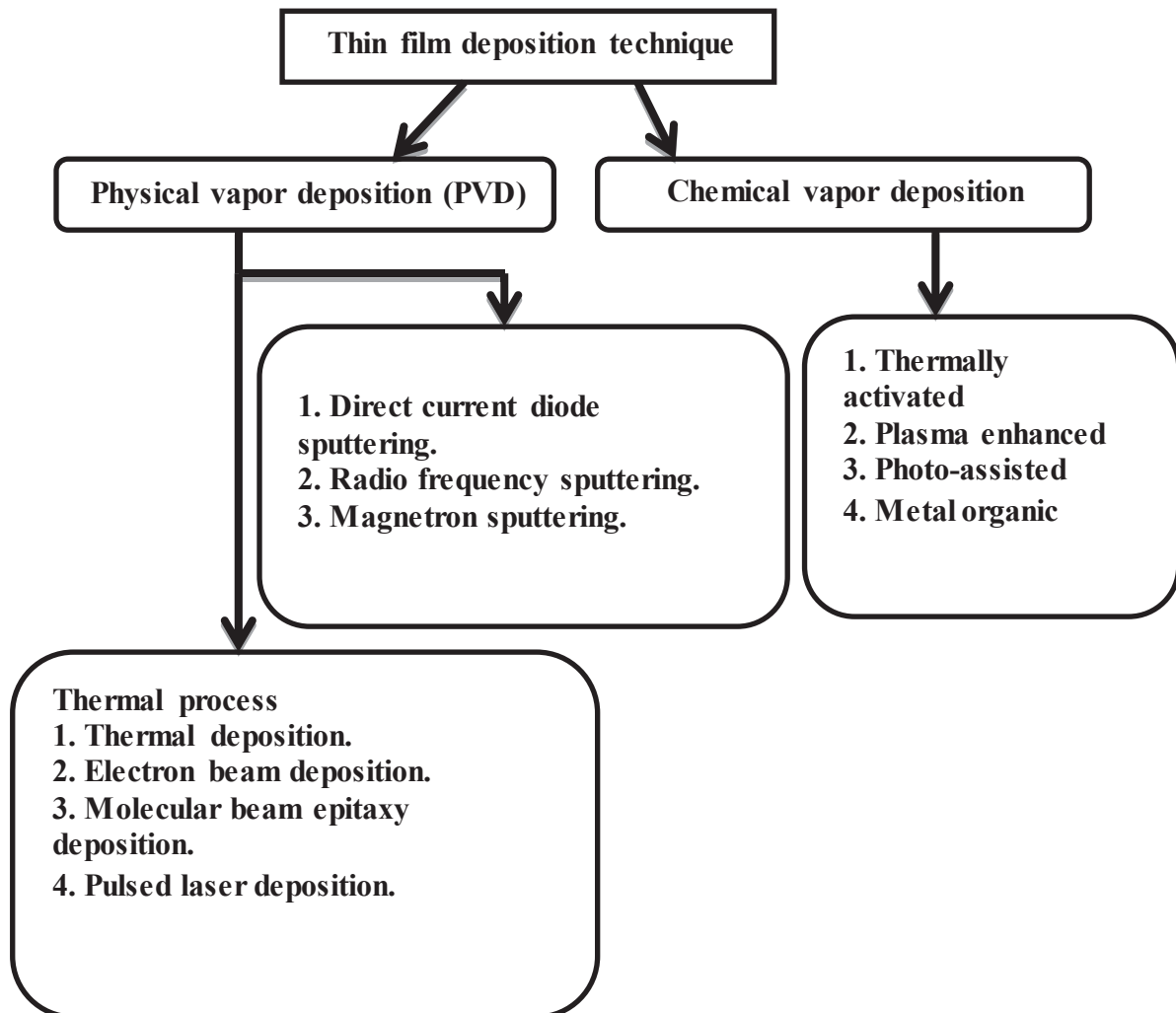


Figure 1.1: Shows the classification of deposition techniques for thin films [43].

1.8 Classification of Physical Vapor Deposition Techniques

In physical deposition methods, atoms are transported directly in a gas phase deposited from the source material onto the substrate forming a thin layer of solid.

1.8.1 Thermal evaporation techniques

Thermal evaporations techniques are simple, convenient and extremely used method for the manufacture of thin films. In this method, materials are vaporized by heating them to a sufficient, high temperature and then condensations of the vapor onto a relatively cooler substrate yielding a thin solid film. Thermal evaporation may be performed directly or indirectly by a variety of physical techniques. Several variants include (a) resistive heating, (b) exploding wire technique, (c) flash evaporation, (d) arc evaporation, (e) laser evaporation, (f) r.f. heating and (g) electron bombardment heating, figure (1.2), represents the working principle of thermal deposition technique.

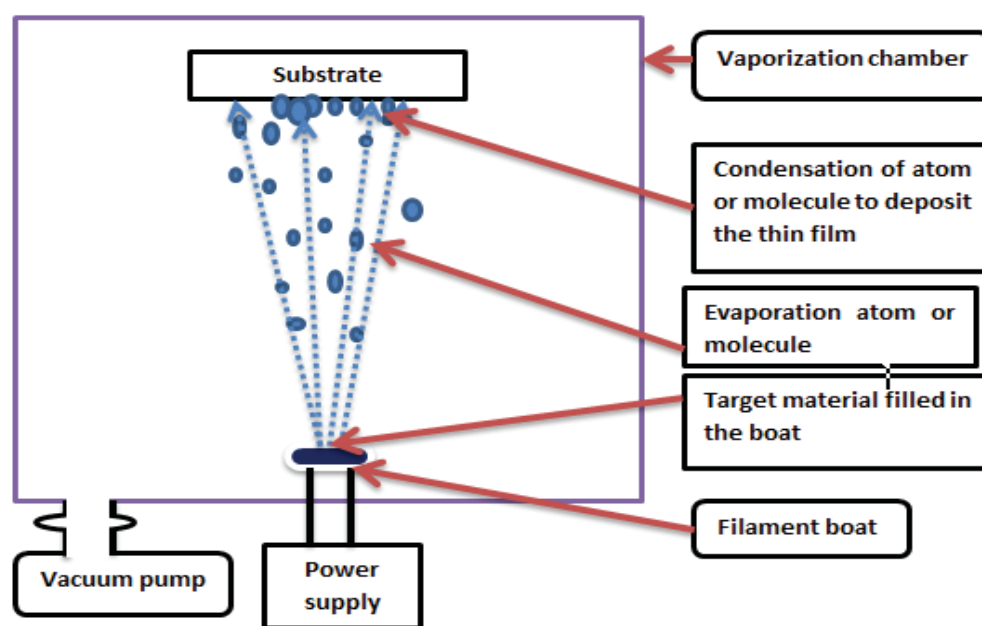


Figure 1.2: Schematic representation of thermal evaporation system [44].

1.8.2 Sputtering

The ejection of atoms from the surface of a material by bombardment with energetic particles is called sputtering [45]. If ejection is due to positive ions bombardment, it is referred to as cathode sputtering. Thin films resulted in the ejected or sputtered atoms which are condensed on a

substrate [46]. The improved technology and new variants of sputtering arrangements have now revived the high pressure sputtering, as a versatile and powerful deposition technique is used for both research and production purposes.

1.9 Growth Mechanism of Thin Film by PVD Technique

The vaporized atoms or molecules from the target material deposited towards on the substrate inside the vacuum chamber by a physically process. At the first, the adsorbed atom (ad atom) has its own energy transferred to the atom during vaporization and then reaching the substrate surface. However, in most of the PVD processes, the substrate is kept at higher temperatures during the deposition. Also, the (ad atom) arriving on the substrate undergoes migration either by its initial energy or substrate energy or a combination of both energies. There are different process parameters of PVD, such as substrate temperature, deposition rate, and residual gas pressure influencing the migration energy of the adsorbed-atom during the growth process of the thin films [47, 48]. Various growth mechanisms involved in the formation of the thin film, such as Island growth (Volmer Weber), Layer-by-layer growth (Frank–van der Merwe) and Stranski–Krastanov (mixed growth).

1.9.1 Island growth (Volmer Weber)

Island growth of the thin films takes place when the vaporized atoms (source) have a strong bonding with each other compared to the substrate surface. This strong bonding within the atoms leads to the formation of localized clusters (Island growth) on the substrate surface. This localized cluster continues to nucleate with the deposition until the exist once of the exposure of the substrate surface. When completely occupying the entire substrate surface, these nucleated clusters join with each other leading to

the coalescence by the minimization of the surface energy to form a continuous thin film, as shown in figure (1.3).

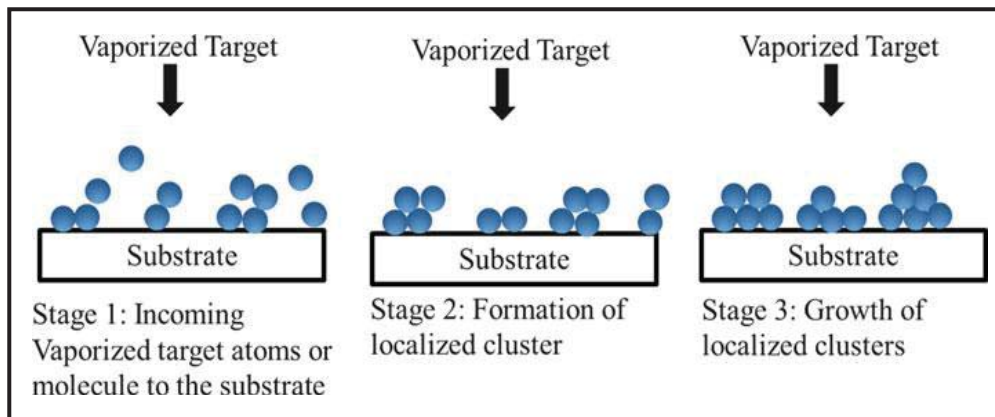


Figure 1.3: Growth mechanism of thin film deposition by Island growth (Volmer Weber) mode [47].

1.9.2 Layer-by-layer growth (Frank–Van der Merwe)

This type of growth of the thin films occurs when there is a strong bonding between the vaporized atoms with the substrate surface compared to the bonding level between each other. This growth process undergoes a sequential formation of layer driven by the lower surface energy of substrate with the (ad atom). Therefore, the formation of a new layer starts after the completion of the first one, as shown in figure (1.4) [44].

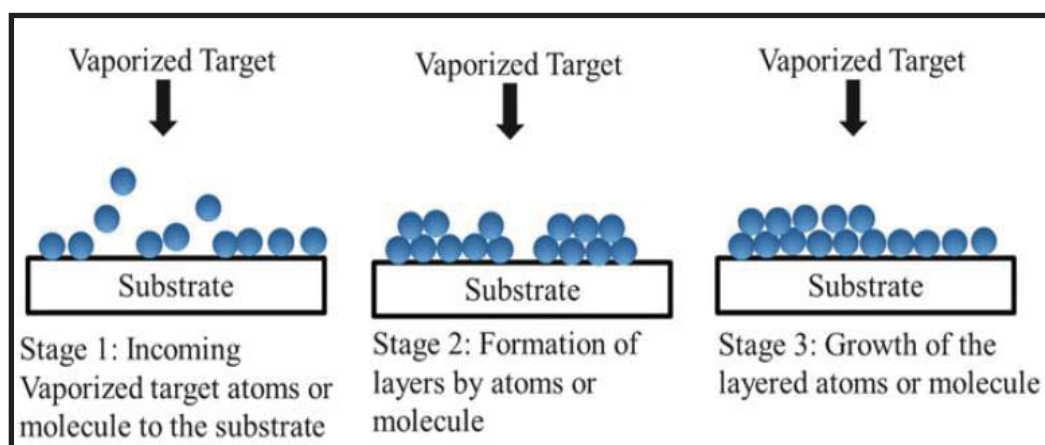


Figure 1.4: Growth mechanism of thin film deposition by layer-by-layer growth (Frank–van der Merwe) mode [44].

1.9.3 Mixed growth (Stranski–Krastanov)

The combination of both "layer-by-layer and island growth leads to Stranski– Krastanov growth mode in the formation of the thin film". Firstly, the ad atom nucleates to form the thin film by means of a two-dimensional layer-by-layer growth mode and then the thin film transforms into a three-dimensional island growth mode, The mechanism of "Stranski–Krastanov growth mode" undergoes three steps. At the first step, the ad atom arrived the substrate undergoes a "layer-by-layer" growth mode and leads to the formation of the metastable island over the substrate. In the second step, these metastable islands grow up and stabilize after overtaking the critical thickness. At the third step, further arrival of ad atom leads to the formation of the island over the stable island and continues this operation to compose of the thin film, as shown in the figure (1.5).

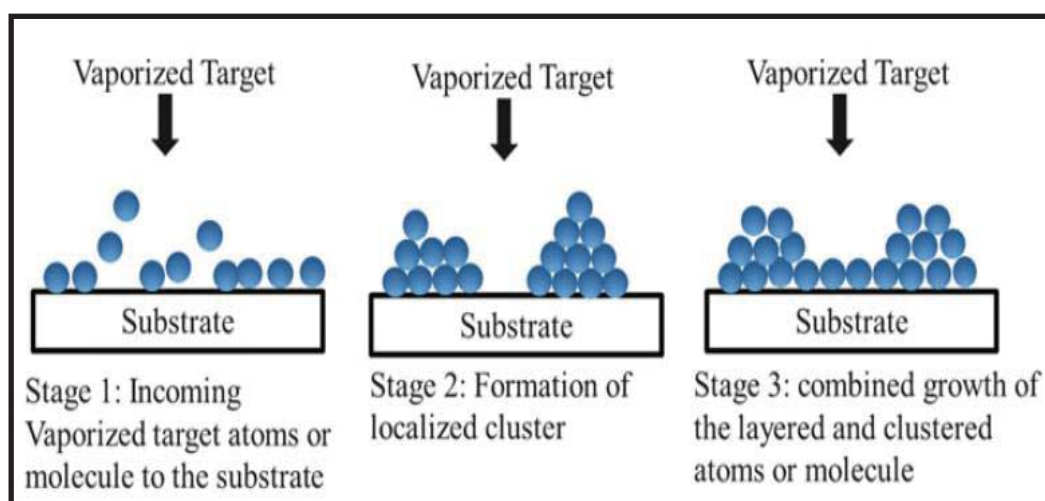


Figure 1.5: Growth mechanism of thin film deposition by Stranski–Krastanov (mixed growth) mode [49].

1.10 Chemical Vapor Deposition (CVD)

The "chemical vapour deposition (CVD) technique" includes the reaction of vapor phase chemicals on the substrate to produce a metal film for different applications. Organic and inorganic materials can be manufactured as thin film in the CVD technique. This technique is used to deposit a solid product onto different substrates by means of a gas phase or surface reaction. It's widely used as a versatile technique to coat large surface areas in a short time and can be determined as a process, in which the gaseous chemical reactants are transported to the reaction chamber [50]. The four steps including different CVD process are shown in figure (1.6). In the first step of reaction, the reactant gas and the carrier gas are introduced into the reaction chamber in a required flow rate. In the second step, the adsorption of reactant gas takes place over the substrate, over which the reactant gases undergo a chemical reaction activated by the thermal energy or ionized plasma. In the third step, these gases undergo surface diffusion and decomposition on the substrate, which leads to the formation of nucleation sites. In the fourth step, a by-product formed on the substrate undergoes desorption and is carried out through the outlet of the reaction chamber. The quality of the thin film formation is determined by the thermodynamics and kinetics of the chemical reaction, substrate temperature, flow rate of the gaseous reactant and physical-chemical properties of the substrate. [44].

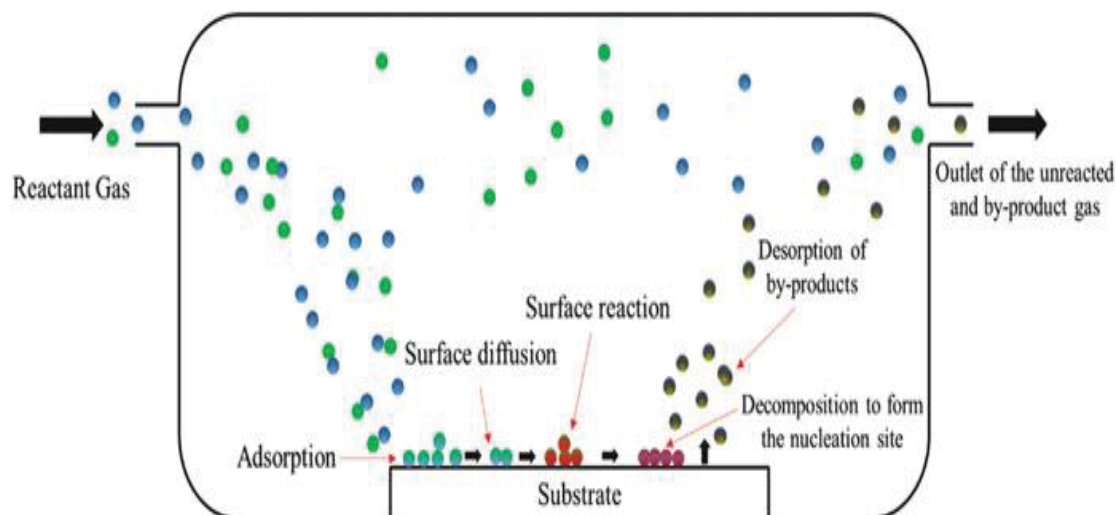


Figure 1.6: Schematic representation of the basic steps in CVD process involved in the formation of thin film [44].

1.11 Hydrothermal Deposition Technique

The hydrothermal is a technique of synthesis materials from low-temperature solution and low cost for the perpetration of thin film. This technique is more environmental friendly and saves energy due to that the various reactions will be done from closed system conditions [51]. The advantage of this technique is suitable to produce a nanomaterial at a low temperature and very simple. Also, this technique is more suitable to control the shape and the size of nanophases. The following some important rules which must be considered for nucleation using this technique:

a) Role of hexamethylenetetramine (HMTA)

(HMTA) plays a very important role for the growth of nanorod thin films. It acts as a weak base and slowly hydrolyzes to give OH^- ions, which help to precipitate Zn^{2+} ions in a high pH medium. The appropriate ratio of pH is between 7-8 for the growth of ZnO nano rods thin film [52].

b) Role of seed layer

Deposition of the seed layer improves the adhesion properties in the nano rods (NRs) as well as the results in the NRs aligned vertically. The seed layer was created by drop casting hydro thermal, this method is simple and low temperature (low cost). Zn was expected to self-oxidize to (ZnO) and function as the seed layer for the hydrothermal growth of (ZnO) NRs. Here are some other factors that effect on the growth of the structure of thin film.

1- Effect of solution concentration. The morphology and diameter of the (ZnO) nanostructures prepared with the (HMTA) hydrothermal method are closely dependent on the amount of concentration of materials available in the solution, by increasing the concentration of the materials in the solutions, the average diameter of the nanorod thin films increases as well.

2- Effect of growth temperature. The temperature gives control on the morphology of the ZnO NRs. For nanoscale growth, the low temperature is always convenient because, at high temperatures, the high thermal energy causes faster adsorption and regeneration, leading to dense and short NRs. At low temperatures, the atoms of the reactive reactants do not have enough energy to propagate through the substrate, so they merge and sit on the surface of the substrate, leading to the formation of many nanostructures [53].

3- Effect of growth time. Based on the results of the different experiment for preparations of metal oxide thin films by hydrothermal, a new series of experiments was conducted with various solution concentrations at a low temperature and a longer growth time to obtain (ZnO) nanowires thin film [53]. This indicates that the high growth temperature and prolongation of growth time, here up to 16 h or more, play an important role in growing (ZnO) nanowires thin film.

1.12 Literature Review

Ji et al in 2005 [54]; deposited SnO₂ films on glass substrates by "atmospheric pressure chemical vapor deposition (APCVD) technique". The results of XRD and AFM revealed that the SnO₂ films were rutile structure, and the grain size was about 1000 nm. The preparation, structure, and photoluminescence (PL) properties of the SnO₂ films were investigated. A violet (396 nm) and a blue (446 nm) photoluminescence peaks were observed at room temperatures. With increasing the annealing temperature, the intensity of the (PL) peaks decreased.

Kambe et al in 2006 [55]; prepared TiO₂-overcoated SnO₂:F transparent conductive oxide films "by atmospheric pressure chemical vapor deposition (APCVD)". Fabrication of a-Si thin film solar cells on SnO₂:F films over coated with TiO₂ films of various thicknesses (1.0 to 2.0 nm). The TiO₂ film deposited by APCVD techniques showed a refractive index of 2.4 at 550 nm, while an increase by 3% of the conversion efficiency for a-Si solar cell fabricated on the 2.0 nm TiO₂ over coated SnO₂:F film, which is refers to an increase in open circuit voltage of 30 mV.

Outemzabet et al in 2007 [56]; conducted the preparation of antimony doped tin oxide SnO₂: Sb thin films by atmospheric pressure chemical vapour deposition (APCVD) method at the substrate temperature changing between (350 - 420 °C) in a horizontal reactor, from a mixture of hydrated SnCl₂, SbCl₃ and O₂ gas. The films which were grown on glass substrates and onto polished and porous n-type silicon, doped the films fabricated with different Sb (Sb/Sn %) contents ranging from (0 - 4%). The films displayed usual cassiterite diffraction pattern with a high crystalline structure. The test of scanning electron microscopy (SEM) of the films are showed textured made up of many pyramidal crystallites with nanofaceted surfaces, referred to highly stabilised material. The

grain growth depends directly on concentration of doping and conditions of deposition. The varied variations of both the transmittance and resistivity are related to the concentration of antimony atoms which induced variation in the size and microstructure of SnO₂ nanograins in the range of (20–40nm). It was clearly seen from SEM observations that the substrate did not affect the morphology.

Yao et al in 2008 [57]; used a gas phase mixture of SnCl₄ and H₂O as a substrate at temperature 550°C for the deposition of tin oxide on Ti substrate by "chemical vapor deposition (CVD) technique. The electrochemical and physicochemical properties as well as the electrocatalytic activity of the (Ti/SnO₂) electrodes prepared were investigated. It was shown that the new electrodes had a compact microstructure, high overpotential for oxygen evolution, and superior activity for pollutants oxidation..

Yu et al in 2008 [58]; prepared ZnO thin film on a glass substrate by Laser plus deposition method. The effect of the substrate temperature on the electrical, magnetic and optical properties of nitrogen-doped ZnO thin films was investigated. It showed that the high substrate temperature depresses the deposition rate and produces much thinner films displaying more robust ferromagnetism. On the other hand, at different substrate temperatures, produces thin films with different nitrogen concentrations, oxygen vacancies, and film thicknesses, leading to produced different electrical and magnetic properties.

Morales et al in 2008 [59]; achieved the deposition of SnO₂ thin film on glass substrate by "atmospheric pressure chemical vapor deposition (APCVD)" using tin tetrachloride as the tin precursor, water vapor and O₃–O₂ as oxidizing agents. The varied substrate temperatures from 200 to 350°C revealed that the temperature of deposition and the oxidizing agent are associated with the structure, resistivities and optical transmission of

the thin films. Finally, good transmission percent films obtained between (85- 90%) in the visible spectrum and lower resistivities ranged from (0.1- 0.020 Ω cm).

Lee et al in 2008 [60]; prepared SnO₂ thin films (nanorod) via "plasma-enhanced chemical vapor deposition (PECVD)". The SnO₂ nanorode thin films were surface modified with nanoparticles of Pd and their sensing properties towards ethanol and H₂ gas were studied. It was shown that the SnO₂ doped with Pd nanorod thin film sensor exhibited 6 and 2.5 times better than undoped sample response to 1000 ppm H₂ and ethanol at 300°C.

Lagha et al in 2009 [61]; performed the deposition of tin oxide SnO₂ on a silicon substrate prepared via the technique of "Atmospheric Pressure Chemical Vapor Deposition (APCVD)". Si-SnO₂ heterostructure obtained and used for photovoltaic (P-V) application. The tin oxide that prospered the thin films deposited via (APCVD) technique depends on three parameters, which are the deposition temperature, oxygen pressure and time deposition. The optimal value of each parameter was obtained by the measurement of the open-circuit voltage of the obtained Si-SnO₂ heterostructure. The tin oxide thin layers obtained exhibited the best optoelectronic and morphology characteristics, at the temperature of 490 °C during 12 min of deposition time under oxygen pressure of 1 bar. The Si-SnO₂ heterojunction solar cell with an area of 2×1.5 cm² is the current-voltage (I-V) measurement characterized, and gives an open circuit voltage of 0.45 V with a short circuit current of 74 mA.

Sheel et al in 2009 [62]; developed an "advanced atmospheric pressure chemical vapor deposition (APCVD) process", to deposits TCOs and in particular doped SnO₂ thin films. The deposited films were characterized for morphology (roughness), crystallinity and resistance to aid the optimization of material suitable for solar cells. Low absorption losses,

less than 1% around 500 nm for 1 pass, were displayed by the optical measurements on these samples, they are lower than those of industrially available TCOs. Selected samples were then used for fabricating single amorphous silicon (a-Si: H) solar cells, they showed high solar energy conversion efficiencies up to (8.2%) and high short circuit currents of (16 mA/cm²). The TCO coatings depicted good performance resulting in a high quantum efficiency yield for (a- Si: H) solar cells.

Pacio et al in 2010 [63]; Deposited Zinc oxide (ZnO) thin films on glass substrates "via atmospheric pressure chemical vapor deposition (APCVD)" technique, using zinc acetate (Zn(CH₃COO)₂) as a precursor of Zn. The structural and optical properties of ZnO films were investigated in different deposition temperatures (300–375 °C in steps of 25 °C). X-ray diffraction analyses showed that the structure of the film polycrystalline in (100) preferred orientation. the samples showed a transmittance bigger or similar to 80% in the visible region The results of these studies showed that at room-temperature photoluminescence spectrum of all films exhibits a strong peak in the visible region at 492.31 nm.

Graaf et al in 2010 [64]; employed the APCVD technique to prepare of SnO₂:F and investigate the influence of various types of precursors and process conditions on the transmittance, morphology and conductance of the film. It was shown that a high transmittance (80%) and low resistivity (4.0x10⁻⁴ Ω.cm) film can be obtained in combination with an intrinsic surface structure that enhances the light trapping effect.

Igwe and Ugwu in 2010 [65]; prepared tin oxide (SnO₂) thin films on glass substrates by "chemical bath deposition technique, using 5 mls of 1M of SnCl₂·2H₂O and 1ML of 1 M of NaOH solution with triethanolamine (TEA) as the complexing agent. The films were subjected to post deposition annealing under various temperatures, 100, 150, 200,

300 and 399°C. The transmittance was between (57% - 95%), while the reflectance was between (4% - 19%). The band gaps obtained under various thermal treatments were between (1.4-3.2eV). The refractive index was between (0.00 - 3.00). The thickness achieved was in the range of (0.12- 0.14 μ m). These properties of the oxide film make it appropriate for different applications, such as a solar cell fabrication, transparent electrodes for panel displays, gas sensor devices, etc.

Zhao et al in 2010 [66]; prepared pure and Cu-doped SnO₂ thin films, by "aerosol-assisted chemical vapor deposition" for H₂S detection. The response and recovery characteristics were analyzed. The thin film has the response and recovery times of 60 and 90 sec, respectively which were tested at room temperature. The selectivity test illustrated that the film was only sensitive to H₂S and acts no response to CH₄ and CO at all. The relationships between response and gas concentration as well as operating temperature were also discussed in this work.

Saikia1 et al in 2011 [67]; deposited tin oxide (SnO₂) thin films on glass substrates "using atmospheric pressure chemical vapor deposition (APCVD)" technique. The substrate temperature was kept at (400°C – 500°C), during the deposition. XRD pattern showed that the preferred orientation was (110) having tetragonal structure. The optical properties of the films were studied by measuring the absorbance, transmittance and reflectance spectra from wavelength between (254 to 1400 nm), and then the optical constants were calculated. The SnO₂ film transmits around ~ 94% of visible light. The four-probe method and Hall-voltage measurement experiment were used for studying the electrical properties of the films. The films displayed the room temperature conductivity in the range (1.08 \times 10² to 1.69 \times 10² Ω^{-1} cm⁻¹).

Mammana et al in 2011 [68]; deposited tin oxide (SnO_2) films by "atmospheric pressure chemical vapor decomposition (APCVD)" in a cold-wall reactor with tin tetrachloride (SnCl_4) as precursor in a flow of dry nitrogen and methanol (CH_3OH). The deposition was carried out at 430°C on glass ceramic (Schott-Ceran) and alumina, soda lime glass substrates. The thickness measurement of the films varied between (80 and 2400nm). The films were polycrystalline with tetragonal rutile structure shown from x-ray analysis. The resistivity of the SnO_2 films on alumina varied between 2×10^{-3} and $4 \times 10^{-3} \Omega\text{cm}$ for thicknesses between (700 and 2400 nm).

LI in 2011 [69] ;deposited tin oxide (SnO_2) thin films on four types of substrates at two conditions one is at "atmospheric pressure and other is at temperatures of 420°C by chemical vapor deposition (CVD)", to investigate the effects of substrate material and surface roughness on their structure. . A home-made vertical reactor was used for the deposition from $\text{SnCl}_4 + 2\text{H}_2\text{O}$ precursors. The results indicated that the substrate material affected on the crystal size, compactness and predominant planes of SnO_2 films, especially when the material of the substrate has a strong adsorption affinity to the films, and the surface roughness has a biggish effect on the structure of SnO_2 films too. It influenced the crystallization of SnO_2 films.

Natsuhara et al in 2011 [70]; investigated the H_2 additional effect for crystallization of SnO_2 films prepared by the "hot-wire CVD technique". The crystallization of SnO_2 films started at 170°C . The atomic hydrogen assisted the nano crystallization for the depositions of SnO_2 films by the "hot-wire CVD technique". Furthermore, the addition of H_2 gas improved the electrical conductivity up to $5.3 \times 10^3 \text{ S/cm}$. However, these effects were limited in the deposition condition of a small amount of hydrogen.

Addition of much higher hydrogen concentration started the etching effect of oxygen atoms.

Volintiru et al in 2011 [71]; deposited un doped tin oxide (SnO_2) thin films in a stagnant point flow "chemical vapor deposition (CVD)" reactor from a water/tin tetrachloride mixture. The electrical properties of the film changed significantly; ten times more conductive SnO_2 films were obtained, with high mobility values up to $55 \text{ cm}^2/\text{Vs}$ when adding methanol during the deposition process. The investigations on the morphological and structural properties indicated that the main effect of methanol was the densification of the SnO_2 films, which probably improved the electrical properties. The nucleation and coalescence of phases took place very early in all conditions. Below 10 nm, the films were already very conductive, this was very useful to the applications that have strict requirements in terms of film transparency.

Khodair et al in 2012 [72]; prepared un doped zinc oxide nanorods and Fe-doped zinc oxide nanoflowers by "atmospheric pressure chemical vapor deposition (APCVD)" technique. An aqueous solution of zinc acetate $[(\text{ZnCH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ without any catalyst was used. The aqueous solution of iron (III) nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ was the dopant source for the Fe-doped nanoflowers. The undoped zinc oxide nanorods and Fe-doped zinc oxide nanoflowers were deposited on glass substrates at 500°C and 550°C substrate temperatures, respectively by the APCVD system. The X-ray diffraction (XRD) measurements for all samples revealed a highly (002) oriented crystalline structure. The results illustrated that all nanostructures are nanorods and nanoflowers shown from "scanning electron microscopy (SEM)". By the SEM results and the XRD measurements, the size of the nanograins was investigated. All structures containing Zn and O elements for undoped ZnO and Fe for doping state were clearly shown from the Energy dispersive X-ray

spectroscopy (EDS). As well, the surface grains of the Fe-doped samples were homogeneous with less RMS roughness values compared with the as-grown undoped ZnO samples by the AFM analysis.

Olopade et al in 2012 [73]; designed an "atmospheric pressure chemical vapor deposition (APCVD)" technique to deposition the F-doped SnO₂ (FTO) thin films on soda lime glass (SLG) with the aim of growing FTO thin films for the local manufacturing of solar cells. Tin (IV) chloride [SnCl₄] and Hydrogen Fluoride (HF) were used as the precursor and dopant, respectively. To optimize the growth of the (FTO) thin films, the substrate temperature and the deposition time were changed. By means of UV-visible spectroscopy, profilometer, and four-point probe methods, the prepared films were characterized. It was observed that the substrate temperatures and the deposition time affected the optical and electrical properties of the deposited thin films. The solar cells grown with these (FTO) thin films gave efficiencies of 0.13% and 0.28%, respectively.

Maleki and Rozati in 2012 [74]; deposited pure tin oxide films on glass substrate at different oxygen flow rates by "atmospheric pressure chemical vapor deposition (APCVD)" technique. The substrates temperature was kept constant at 500 °C, and. The oxygen with the varied flow rates of (0–400 SCCM) was used for both a carrier gas and an oxidizing agent. The electrical parameters variations evinced showed that these parameters vary with varied oxygen flow rate, reaching an optimum value at the flow rate of (100 SCCM). The X-ray diffraction (XRD) also showed that the structure to be polycrystalline for all samples deposited at different oxygen flow rates. The field emission scanning electron microscopy (FE-SEM) demonstrated a reduction in grain size corresponding to increasing flow rates until (200 SCCM), and after that, with a further increase of flow rate, the grain size increased.

Yates et al in 2013 [75]; used the "atmospheric pressure chemical vapor deposition (APCVD)" technique to deposit F-doped SnO₂ on glass substrate using monobutyl tin trichloride with trifluoro-acetic acid as the dopant source. The deposited films were characterized for crystallinity, morphology, optical haze and electrical properties. Additionally, the stability of the films to the post growth annealing was studied. It was shown that increasing the dopant levels led to a decrease in surface roughness along with a reduction in feature size. Also it was noted that the increased doping gave an increased mobility and carrier concentration, with a non-linear decrease in resistivity. The samples tested depicted only changes in optical and electrical properties at high temperatures, confirming their thermal stability.

Maleki and Rozati in 2014 [76]; deposited pure tin oxide thin films on glass substrates at various substrate angles relative to the source position by "atmospheric pressure chemical vapor deposition (APCVD)" technique. Deposition temperature at 500°C and oxygen flow rate with carrier gas (100 SCCM) were used. Investigation of the sheet resistance showed that the resistivity varies between (106 and 241 Ω/ cm²). X-ray diffraction (XRD) also appeared that the structure was polycrystalline with the preferred orientation of (110) for all films deposited at the various substrate angles. "Scanning electron microscopy (SEM)" images also revealed a uniform and impacted structure on the surface of all samples.

Karuppiah et al in 2015 [77]; prepared zinc oxide nanorods and copper oxide nanospheres (ZnO–CuO), through a "simple hydrothermal technique". Presence of polyethylene mine formed the nanorods and nanospheres which acts as a stabilizing or a reducing agent for the growth of nanocomposite and makes them more stable. The obtained nanocomposite was confirmed by "scanning electron microscopy, energy

dispersive X-ray spectroscopy, X-ray diffraction and cyclic voltammetric studies". The (ZnO–CuO/GCE) showed an extremely good electrocatalytic. The sensor exhibited showed the high sensitivity of ($1457.5 \mu\text{A mM}^{-1} \text{cm}^{-2}$). However, the (ZnO–CuO/GCE) is able to reveal the glucose even in the presence of biologically interfering molecules. The sensor achieved appreciable repeatability, long term stability and reproducibility (up to 38 days). The sensor was demonstrated practically in the human serum samples.

Lu et al in 2016 [78]; Synthesized SnO_2 nanoparticles by a simple hydrothermal technique, via using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, hexamethylenetetramine, and trisodium citrate in water for 12 h at 120°C . The effects of surfactant and precipitant on the SnO_2 nanoparticles. Were investigated SnO_2 nanoparticles were synthesized in the temperature range ($120\text{-}180^\circ\text{C}$) with long reaction time in the presence of trisodium citrate. It was shown that it is difficult to get SnO_2 nanoparticles at 120°C in the presence of trisodium citrate. The crystallinity of SnO_2 nanoparticles with an average size of about 5 nm has good sensitivity to acetaldehyde and ethanol due to their smaller particle size.

Noh et al in 2017 [79]; prepared (SnO_2) thin film at different temperatures by "aerosol-assisted chemical vapour deposition (AACVD)" technique. The deposited SnO_2 thin film at a high temperature exhibited a higher crystallinity, higher light absorption, rougher surface and greater free-carrier density in comparison to low temperature processed counterpart. It was shown that the photocurrent density of PEC cells based on high temperature (450°C) processed SnO_2 layer was about $27 \mu\text{A}/\text{cm}^2$ at 1.0 V, approximately five times greater than that of SnO_2 layer prepared at low temperature (180°C). On the other hand, the low temperature-based SnO_2 ETL was noticed to increase the efficiency of the organic solar cells by about six times in comparison to their high

temperature based counterparts. The reasons for such phenomenon lay in the morphological, optical and electrical properties of the fabricated SnO₂ layer.

Al-Sarraf et al in 2018 [80]; successfully synthesized ZnO nanostructures as nano tripods and Fe-doped ZnO nano flowers on glass substrates by "atmospheric pressure chemical vapor deposition (APCVD)" technique, with an aqueous solution method. And the effect of (Fe doping) concentration on the structural properties of the films was studied. The samples were prepared inside the reactor of the APCVD system. The formation of nanostructures during the film growth and the size of the nano grains were investigated by Scanning electron microscopy (SEM). The "AFM" analysis indicated that the surface grains of the Fe-doped samples are homogeneous with RMS roughness values about 32 nm which is less than un-doped ZnO thin films. "Energy dispersive X-ray spectroscopy (EDS)" viewed that all structures contain Zn and O elements for un doped ZnO and Fe at the doping state.

1.13 Objective of the Study

Due to the recent scientific development in the field of manufacturing nanomaterials and their various applications in all scientific fields and the need of this kind of research studies, especially in our country, in this field, the current study was done according to the following scientific steps.

- 1- Synthesis of (SnO₂ and ZnO) nanostructure thin films by changing the deposition conditions to obtain the best crystalline structures.
- 2- Using the "atmospheric pressure chemical vapor deposition (APCVD)" and simple and low cost hydrothermal drop casting techniques for preparing the different structures of (SnO₂ and ZnO) thin films.

- 3- Study the characteristics of (SnO₂ and ZnO) nanostructure thin films.
- 4- Evaluation of the use of (SnO₂ and ZnO) nanostructure thin films in some applications such as gas sensing detectors.