

Synthesis and Fabrication Techniques of ZnO Thin Films for Gas Sensing: An Overview

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In this review paper attention will be centered on the various synthesis techniques of ZnO thin films, because the synthesis process directly affects the cost and flexibility in the production of gas sensing equipment. ZnO is our choice because it is a versatile material with outstanding electrical, optical, and chemical characteristics. Due to their strong sensing response, simple fabrication, long-term stability, and cost-effectiveness, ZnO-based thin films are a good choice for a gas sensor that has attracted a lot of attention due to their versatility in applications such as gas sensors, microelectronics, solar cells, and optoelectronics industries. Thin films have a wide range of qualities specified by film thickness, morphology, structural properties, and composition, which are required to fulfil the necessities of a broad range of diverse applications. This article aims to provide a broad research status of various synthesis processes of ZnO thin films.

Keywords: ZnO, Physical Techniques, Chemical Techniques, Gas Sensor, MOx, Gas sensing, Nano materials (NPs), Nanotechnology.

1. Introduction

Rapid rise of industrialization and urbanization have caused critical air pollution. Air pollution is an indicator of environmental changes that impact health and human being. It also affects plants and materials and has been attributed to emissions from industries, vehicles, and kitchens and waste decay besides the emission from natural sources viz., soil erosion, sea spray, forest fire, volcanoes etc. Air pollution causes global warming, climate change and affects human being and environment directly and indirectly (J. Zheng et al., 2009).

ZnO has a number of advantages over conventional metal oxide-based gas sensors, including low cost and non-toxicity in nature, making it environmentally acceptable. ZnO-based gas sensors are widely used in a variety of applications because of their excellent sensing response, superior selectivity, ease of manufacturing, low cost, good thermal and chemical stability, and non-toxicity. Furthermore, with a bandgap of 3.37 eV and a significant exciton binding energy of 60 meV (Rai et al., 2012; J. Zheng et al., 2009). It has seen an enormous exploration of metal oxide semiconductor-based gas sensors that have great properties of an ideal gas sensor throughout the last few decades. SnO₂, ZnO, WO₃, Fe₂O₃, and CuO with various morphologies like thin films, nanoplates, nanowires, nanorods, nanoflowers, nanoneedles, and nanoribbons have all been investigated as metal oxide based gas sensors (P. Dwivedi et al., 2017; Nunes et al., 2019; Umar et al., 2017; Vallejos et al., 2018). Sensing response of the gas sensor depends upon the dimension of nanostructures. By using various synthesis methods, numerous types of morphologies and nanostructures can be achieved. As synthesis methods for achieving the necessary morphologies and nanostructures, spray pyrolysis, sol-gel, dip coating, spin coating, chemical vapour deposition (CVD), radio frequency (RF) sputtering, template synthesis method, molecular beam epitaxy, and hydrothermal deposition have all been examined (Baratto, 2018; Mondal & Sharma, 2016; Studenikin et al., 1998; Yang et al., 2013; Znaidi, 2010). Table 1 shows successfully Zinc oxide deposition via the different synthesis process. Several studies on the fabrication of Zinc oxide films using various techniques have been conducted. The goal of this project is to provide a quick overview of unique ZnO thin film processes.

Table 1: Various types of ZnO morphologies and nanostructure grown by different synthesis techniques

ZnO Nano Scale	Substrate	Deposition Technique	Reference
ZnO thin film	Quartz	MOCVD	(Pati et al., 2013)
ZnO thin film	Sapphire	Sol-gel	(Chia et al., 2013)
ZnO nanoflowers	Al ₂ O ₃	Hydrothermal	(Song et al., 2019)
ZnO nanorods	Silicon	RF magnetron sputtering	(Sundara Venkatesh et al., 2014)
ZnO nanofibers	SiO ₂	Electro spinning	(Aziz et al., 2018)
ZnO nanowires	Zn Seed layer	CVD	(Rodwihok et al., 2019)
ZnO layer	Sapphire	MBE	(El-Shaer et al., 2005)
Al-ZnO thin film	Glass	Spray pyrolysis	(Kolhe et al., 2018)
ZnO thin film	Soda lime glass	Electron beam	(Ani et al., 2020)
ZnO thin film	Soda lime glass	Atomic layer deposition	(Tammenmaa et al., 1985)

2. Various thin film deposition techniques

Thin films have an amazing impact on today's modern technology. Because of the significant support they provide to these applications, they operate as a spine for advanced applications in several domains such as optical devices, environmental applications, communications devices, energy storage devices, and so on (Nwanna et al., 2020). All of the critical challenges in thin film applications are caused by morphology and stability. The deposition procedures have a strong influence on the shape of thin films. Thin films can be deposited using both physical and chemical methods (Znaidi, 2010). Spray pyrolysis (Omura et al., 1999), Sol-gel (Thiagarajan et al., 2017), Dip coating (Ray et al., 1998), Hydrothermal synthesis (Suchanek & Riman, 2006), Pulsed laser deposition approach (J. J. Park et al., 2015), Spin coating (Ilican et al., 2008), chemical vapour deposition (CVD) (Hwang & Lee,

2010) , and Atomic layer deposition systems (Levy et al., 2008) are some of the advanced thin film deposition techniques and ideas covered here. These days, so many technologies are utilized for reducing the materials into nano-size and nano-thickness. This reducing behaviour of materials into nano-materials leads to the innovation of new and unique behaviour in optical, electrical, optoelectronic, dielectric applications, etc. Thin films or coatings, a new branch of material science, are a thin layer of materials in which the thickness differs from nanometres to micrometres. Just like all other materials, the structure of thin films or coatings is categorized into two main types, which are: amorphous structure and polycrystalline structure. These structures formation relies upon preparation condition and nature of materials. The two parts of the thin films include: the layer and the substrate. Here we will discuss about different type deposition techniques of thin films:

2.1 Spray pyrolysis-Spray pyrolysis is one of the advanced techniques of thin film deposition that consists of chemical reduction approach in which for the production of finished product, endothermic thermal disintegration occurs on the heated area of the substrate. Spray pyrolysis is the process of formation of chemical compound layer on the surface of heated substrate by spraying a solution. The metallic compounds that this technique uses are either dissolved in a liquid mixture or sprayed by a spray nozzle on pre-heated substrate accompanied by gaseous substance.

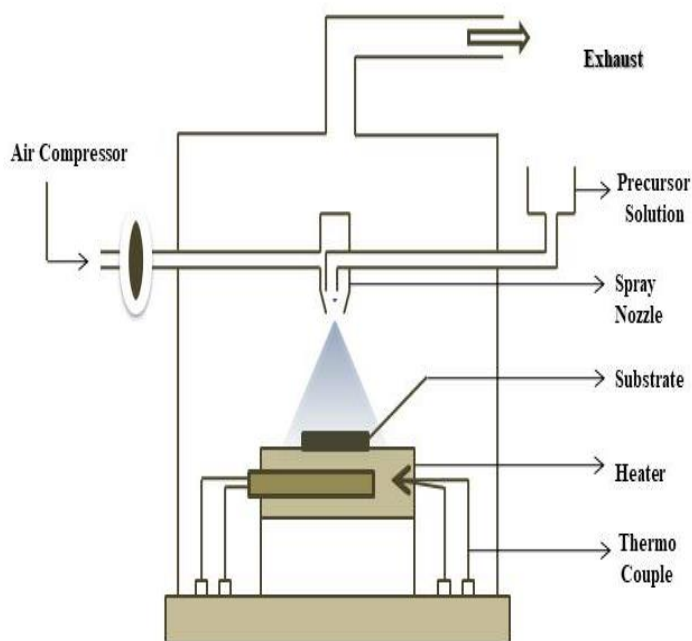


Figure 1: Schematics of Spray Pyrolysis set up

The spray pyrolysis can be controlled by the parameters such as: temperature of the substrate, thickness, concentration of the solution, air flow rate through the nozzle, nozzle

substrate distance and solution composition (Filipovic et al., 2013) Spray pyrolysis is a chemical solution technique that generates the completed product by producing endothermic thermal disintegration on the heated surface of the substrate utilising a chemical reduction strategy (Nwanna et al., 2020). There have been various reports on the fabrication of Zinc oxide thin films using the Spray pyrolysis technology, such as Zinc oxide (ZnO) thin films generated on a glass substrate using an aqueous solution precursor of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) by Mani et al. (Mani & Rayappan, 2014). A variety of processes was used to characterise the prepared thin film for various properties. The deposited films were polycrystalline with a wurtzite crystal structure, according to X-ray diffraction (XRD) analysis. Using Scherrer's formula, the average crystallite size for ZnO thin films was found to be 28 nm. SEM (Scanning electron micrographs) clearly show that morphology of ZnO thin films contain uniformly dispersed and firmly packed spherical grains with distinct grain boundaries. Another study by Shewale (Shewale & Yu, 2016) investigated Un-doped and Ti-doped ZnO thin film for H_2S gas sensing properties prepared by chemical spray pyrolysis on the glass substrate. According to XRD analysis the films are polycrystalline zinc oxide with a hexagonal wurtzite structure, and the 2 wt% Ti doping resulted in the best crystallinity. FE-SEM investigations corroborate the XRD findings, revealing polygonal granular surface morphology for 2 wt% Ti doped ZnO films with high grain sizes. The H_2S gas sensing properties of all the films are investigated finally At 200°C operating temperature, a 2 wt% Ti doped ZnO thin film exhibits a maximum gas response (0.29) to 20 ppm H_2S gas exposure and shows strong selectivity over other organic gases. Table 2 summarises several key studies on the ZnO-thin films based gas sensor using the spray pyrolysis technique.

Table.2 Spray pyrolysis for the growth of the ZnO based thin film for gas sensing.

Material	Nano type	Substrate	Target gas	Reference
ZnO	Thin film	-	Alcohol	(Singh et al., 2012)
ZnO	Thin film	Glass	NH_3	(Mani & Rayappan, 2014)
ZnO	Thin film	Glass	Ethanol	(Tarwal et al., 2013)
ZnO	Thin film	Glass	CO_2	(Hunge et al., 2018)
Mg-ZnO	Thin film	Glass	NH_3	(Kulandaisamy, Reddy, et al., 2016)
Co-ZnO	Thin film	Glass	Acetaldehyde	(Kulandaisamy et al., 2016)
ZnO	Nanorods	Glass	H_2S	(Shinde et al. 2012)
Cu-ZnO	Thin film	Glass	H_2S	(Shewale et al., 2013)
In-ZnO	Thin film	Soda lime glass	Methanol	(Bharath et al., 2018)
Al-ZnO	Thin film	Glass	H_2S	(Badadhe & Mulla, 2011)

2.2 Sol-gel- Another technique of thin film deposition is sol-gel technique. It is a flexible wet chemical process. It is used for the preparation of innovative materials like ceramics and inorganic-organic hybrid materials. Basically, this method includes transition of solution to semi-solid phase. In simple words, it is the conversion from liquid sol to sol gel. The major use of this technique is for the synthesis of nano particles, nano fibres, thin film coating, mesoporous films and materials, and exceptionally porous aero gel materials. In the process of producing a solid solution from small molecules, metal oxide is used (C. Brinker et al., 1992).

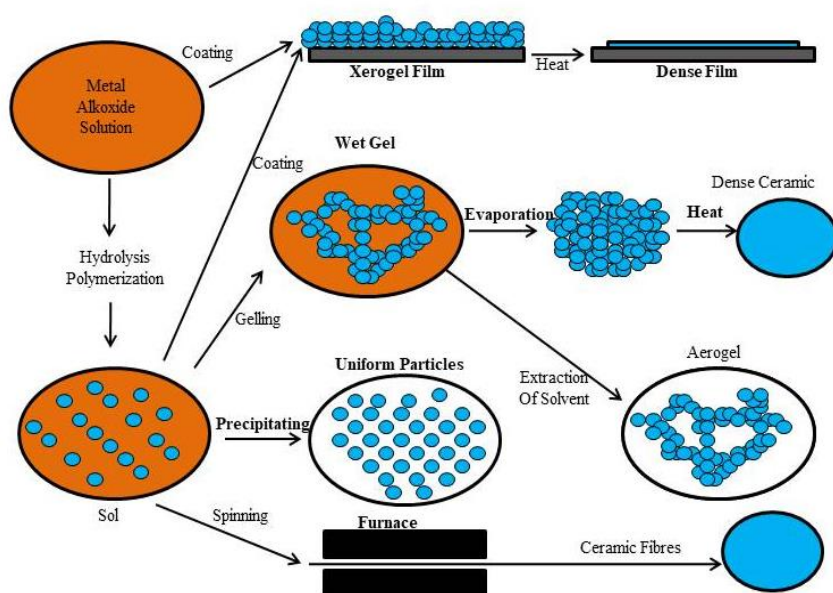


Figure 2: Schematics of Sol-gel process

The sol-gel process (Figure 2) is a saturated chemical reaction in which tiny molecules are used to make solid materials. It's a technique for coating glass or metals with single- or multi-component oxide coatings. It usually requires making a sol from a mixed homogeneous solution, changing it into a gel by the polycondensation process, and then heat treating the substance with respect to the desired material (Schubert, 2015). There have been numerous investigations on the synthesis of Zinc oxide thin films by the help of Sol-gel process. (Khan et al., 2017) Sol-gel is used to build multilayer thin layers of zinc oxide (ZnO) on a glass substrate. Prepared thin film samples with 1, 3, and 5 layers are ready for analysis. The existence of ZnO in these films is confirmed by this XRD pattern. The morphological qualities can be seen in the SEM data. There were no cracks in any of the deposited films, and the grain structure was evenly dispersed. In another study, the development of ZnO thin films utilizing the sol gel approach was analysed (Muthukrishnan et al., 2016). ZnO has been produced effectively utilising a low-cost and simple approach. A detailed characterisation has been completed and described. X-ray diffraction was used to determine the crystallinity and crystallite size of the produced thin film. Using the (002) plane, XRD confirms the presence of hexagonal wurtzite structure, and Peak broadening concludes the production of nano particles and average crystallite size of the film was determined to be 20 nm. The chemiresistive approach was used in the sensing studies, in which the chemical reaction between adsorbed oxygen on the material surface and the target gas results in resistance fluctuation. The response and recovery times for various acetone concentrations are measured in seconds. With a response of 1.08, the lowest detection limit of a room temperature ZnO thin film was found to be 2 ppm of acetone. Table 3 summarises various significant findings on the sol gel technique-based ZnO-thin films based gas sensor.

Table 3: Sol-gel process for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Thin film	Glass	H ₂ S	(Nimbalkar & Patil, 2017)
ZnO	Thin film	Alumina	Acetone	(Kakati et al., 2010)
Cu-ZnO	Thin film	Glass	C ₃ H ₈	(Gómez-Pozos et al., 2016)
Au-ZnO	Thin film	Alumina	NO ₂	(Gaiardo et al., 2016)
Ni-ZnO	Thin film	Glass	H ₂	(Soleimanpour et al., 2013)
Mg-ZnO	Thin film	Glass	Acetic acid	(Khorramshahi et al., 2018)
ZnO	Thin film	Glass	NH ₃	(C.-F. Li et al., 2014)
Al-ZnO	Thin film	Glass	NH ₃	(Aydın et al., 2019)
ZnO	Thin film	Glass	NH ₃	(S. L. Patil et al., 2010)
ZnO	Thin film	Quartz	CH ₄	(Pati, 2017)

2.3 Spin coating technique-Another technique of thin film deposition is spin coating which is the process of depositing thin film on the plane substrate, accompanied by sol gel technique. The sol gel is added upon the substrate at the center to spin the substrate with specific revolution per minute. The coating material spreads over the substrate uniformly because of the centrifugal force. Viscosity, ratio of the solution and the solvent used are some of the factors on which the thickness of the film depends. Fabrication is also done through spin coating technique like, fabricating film layers by the use of prepared sol gel of the needed film material as well as fabricating a uniform thin film in nano scale thickness. Layer by layer spin coating at suitable temperature followed by drying at each step can be highly useful way in achieving required thickness of the film. The films that are already fabricated are expected to evaporate the solvent by heating for few seconds and then finally annealed at a higher temperature to form films. The spin that is maintained up to 20-80 revolutions per second for 30-60 seconds can be useful for obtaining photoresistive thin film layers of 1 micrometer thickness (Tyona, 2013).

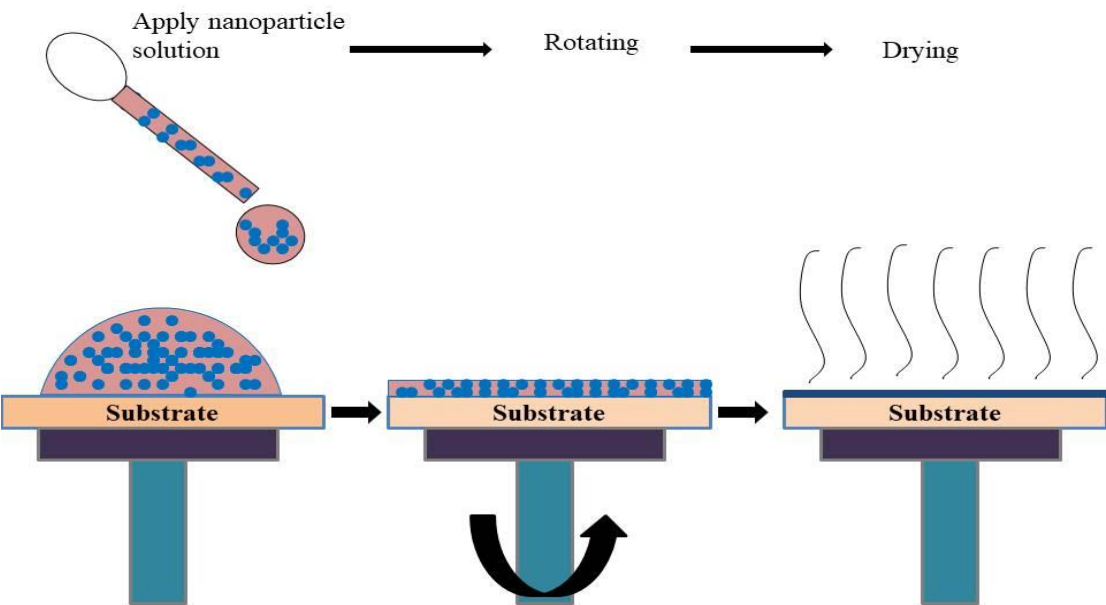


Figure 3: Schematics of Spin coating process

The spin coating approach has been employed in a variety of studies to create ZnO thin films for gas sensing (Rambu et al., 2013). They examined the spin coating on pristine ZnO and Fe-Doped thin film for the gas sensing. The examined films have a polycrystalline structure, according to X-ray diffraction analysis. The structural properties of the films were found to be highly influenced by the Fe concentration in the ZnO host. Ethanol, methane, and acetone sensitivity tests were carried out. The experimental results show that the investigated films are extremely sensitive to acetone, with Fe doping increasing the sensitivity value. An exceptionally responsive gas sensor film was generated, according to their research. Table 4 summarises some of the most important findings from the spin coating technique-based ZnO-thin films gas sensor.

Table.4 Spin coating process for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Thin film	Silicon oxide	Phosphate	(Foo et al., 2013)
Cdo-ZnO	Thin film	Glass	Oxygen	(Rajput et al., 2018)
Y-ZnO	Thin film	Glass	-	(Thirumoorthi et al., 2015)
ZnO	Thin film	Glass	-	(Gadallah et al., 2013)
ZnO	Thin film	Glass	-	(Heredia et al., 2014)
ZnO	Thin film	Hydrophilic glass	Propyl alcohol	(Cheng et al., 2004)
CuO-ZnO	Thin film	ITO glass	-	(Prabhu et al., 2017)
Al-ZnO	Thin film	Glass	H ₂	(Hou & Jayatissa, 2017)
ZnO	Thin film	Glass	NO ₂	(Chougule et al., 2012)
Au-ZnO	Thin film	Glass	Acetone	(Deshwal & Arora, 2018)
Na-ZnO	Thin film	Glass	CO ₂	(Basyooni et al., 2017)

2.4 Dip coating- The process of dipping flat or cylindrical substrate in a solution for the purpose of coating the substrate is known as dip coating. There are various stages involved in this method. Immersion: The process of immersion of substrate at a uniform speed in the material precursor solution. Pull up: Immersed substrate has to be kept in the solution for a fixed duration and then slowly pulling it out from the solution. Deposition: Uniform deposition of thin film layer takes place when the substrate is slowly pulled up from the solution. The thickness of the layer is controlled by the withdrawal rate i.e. faster pull up results in thick layers while slower pull up results in thin layer. The withdrawal rate can be controlled by highly advanced programmable set up. In these programmable set up, the dip time as well as pull up time can be pre-programmed. Drainage: In this stage, the liquid that is deposited in excess is drained from the substrate. Evaporation: Solvent is evaporated and thin layer forms in this stage. In case of volatile solvent, e.g. alcohol, the process of evaporation begins during pulling up of substrate from the solution (C. J. Brinker et al., 1991).

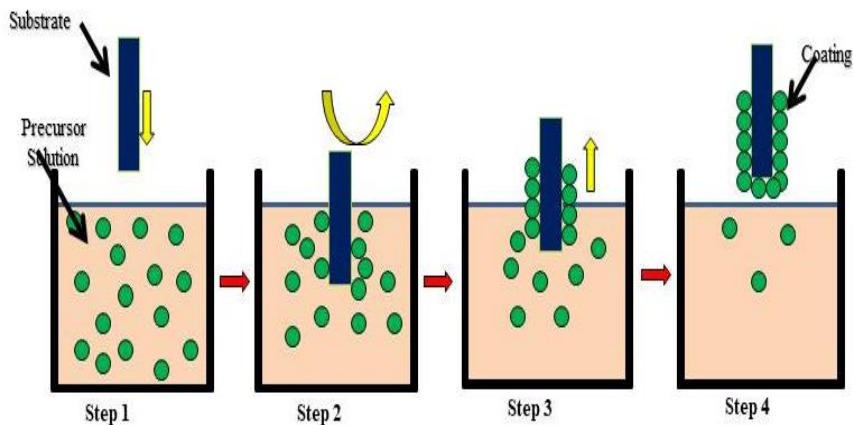


Figure 4: Schematics of dip coating process

We have number of studies that have used the dip coating process to develop a ZnO for the gas sensing. On p-silicon (100) substrates, ZnO thin films are produced using a sol–gel procedure and then dip-coated for use as a hydrogen gas sensor (Dey et al., 2018). The addition of dopants such as Au and Pd used to improve the gas response and electrical properties. At annealed temperatures of 550, 450, and 350 °C, FESEM analysis confirms that Au-modified and Pd-modified grain sizes are smaller than typical ZnO-based thin-film sensors. Furthermore, as compared to pd/ZnO and undoped ZnO thin-film sensors at annealing temperatures of 350°C and 450°C, Au-modified ZnO-based thin-film sensors have showed maximum sensitivity and small grain size at annealing temperatures of 550 °C. This study results appears to be suitable for gas detection. The dip coating technique-based ZnO-thin films gas sensor yielded some of the most noteworthy findings, which are summarised in Table 5.

Table 5: Dip coating process for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
CeO ₂ -ZnO	Thin film	Glass	C ₆ H ₆	(Ge et al., 2007)
ZnO	Thin film	Glass	Monoethnol	(Musat et al. 2008)
ZnO	Nanorod	Glass	SO ₂	(Yulianto et al. 2017)
La-ZnO	Nanocorn	Glass	H ₂	(Venkatesh et al., 2014)
Y-ZnO	Thin film	Glass	NO ₂	(Kılınc et al., 2012)
Fe-ZnO	Thin film	Glass	Ethanol	(Pronin et al., 2014)
ZnO	Thin film	Glass	NO	(Septiani et al., 2019)
ZnO	Thin film	Glass	C ₆ H ₆	(Tian et al., 2012)
In-ZnO	Thin film	Glass	NO ₂	(Bhatia & Verma, 2018)
ZnO	Thin film	Glass	NH ₃	(Vanaraja et al., 2016)

2.5 Vacuum evaporation-In this technique, coating material is evaporated into vapor. Vaporization of coating material takes place by passing high current through the source in vacuum. After that vapor formation of coating material, it gets depozsited on the surface areas of substrate. Tungsten and tantalum are used as charges or boats during the evaporation to keep the source material over them. For the evaporation, resistive heating method is used along with that a typical pressure of 10⁻⁴ – 10⁻⁶ Torr has to be maintained within the vacuum

chamber. In order to prevent the solid particles from reaching the substrate, there is a large distance between the source material and the substrate. High vacuum coating with thermal evaporation process and thin thickness of about $100 \pm 5 \text{ nm}$ is required to prepare thin films of LDH's which are extremely amorphous in nature and can be used as solar cell and transistor. Here are the average direct energy gaps for different nanostructure films (Janarthanan et al., 2021)

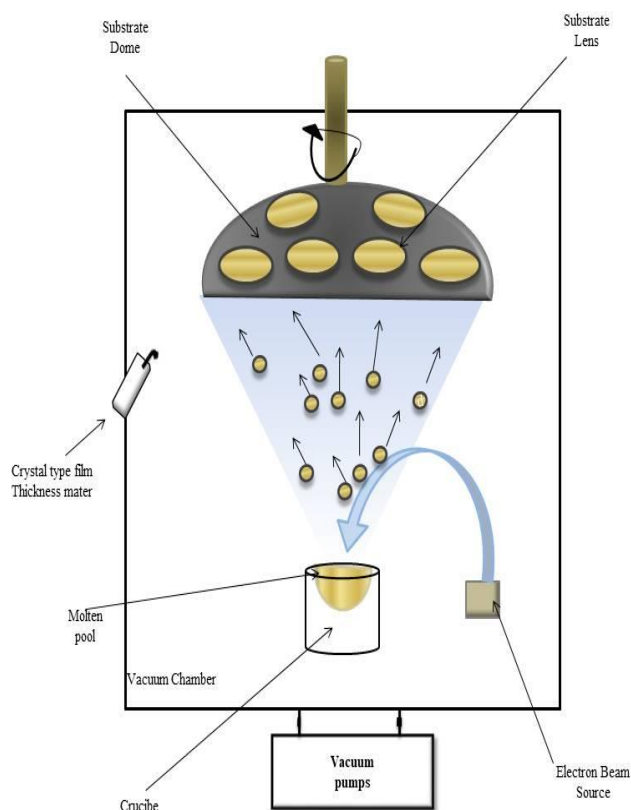


Figure 5: Schematics of vacuum evaporation process

Because of its exceptional interfacial characteristics, vacuum evaporated ZnO thin films for gas sensing are becoming increasingly popular. Dev et al., (Dev et al., 2020) investigated thin films of pure and In-ZnO produced on a glass substrate, they added to the body of information about this deposition process. For acetylene gas sensing, these zinc oxide thin films were made via vacuum evaporation on a glass substrate. The crystalline structure of pure ZnO and In-ZnO thin films is determined using an X-Ray diffractometer. The nature of pure ZnO and In-ZnO thin films is polycrystalline, according to XRD analysis. FESEM, AFM, and FTIR techniques, as well as gas sensing applications, were used to characterise thin films. It also shown that the maximum sensitivity for acetylene gas 3% In-ZnO thin film is 29.06 at 150 °C working temperature for 100 ppm gas concentration. In Table 6, some interesting results are shown for the vacuum evaporation technique-based ZnO-thin films gas sensor.

Table 6: Vacuum evaporation for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Thin film	Glass	LPG	(Iftimie et al., 2008)
ZnO	Thin film	Glass	NO ₂	(Shishiyanu et al., 2005)
ZnO	Thin film	Al ₂ O ₃	-	(Rambu et al., 2012)
ZnO	Thin film	Si	CH ₄	(Sunipa et al.,2017)
ZnO	Thin film	Glass	NH ₃	(Fairose et al., 2017)
MnO ₂ -ZnO	Thin film	Glass	NH ₃	(L. A. Patil et al., 2011)
ZnO	Thin film	Glass	LPG	(Sheeba et al., 2017)
ZnO	Thin film	Si	-	(Hassan & Hashim, 2013)
ZnO	Nanowires	Glass	NH ₃	(A. Kampara et al., 2018)
Cr ₂ O ₃ -ZnO	Thick film	-	NH ₃	(D. R. Patil et al., 2007)

2.6 Electron beam evaporation-Tungsten and tantalum filament produces the electron beam which is deflected by magnetic field (which guides the electron beam from the filament towards the source material) and electric field (which guides the beam over the substrate) ensuring the uniformity in heating as well as formation of vapor. Vapor reaches the substrate and forms the thin layer over the substrate. Various materials require different higher film thickness but the favourable maximum thickness is 300nm (Chrisey & Hubler, 1994).

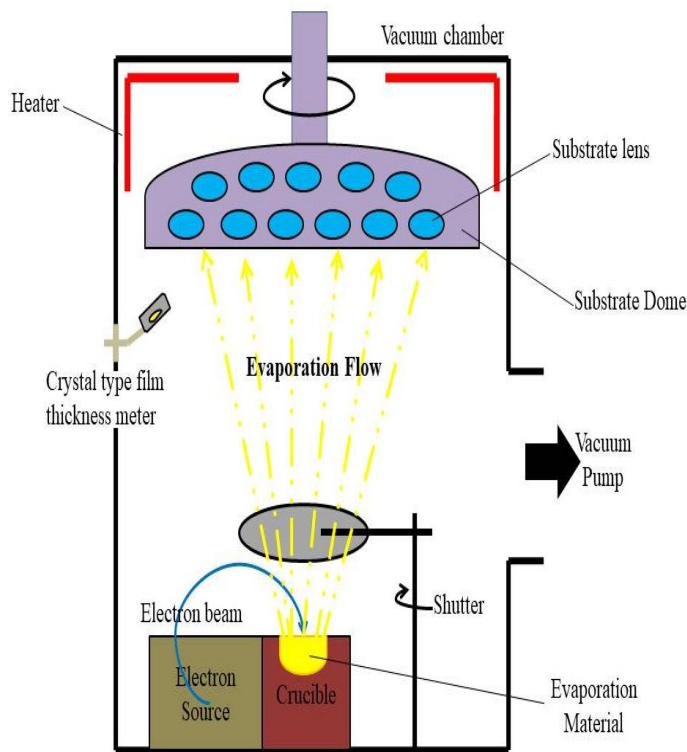


Figure 6: Electron beam deposition process

Field electron emission and thermionic emission might all be used to create electron beams. The formed electron beam increases in kinetic energy and is focused towards the evaporation material; as these electron beams make contact with the evaporation material, the electrons quickly lose their power. Through contact with the material for evaporation, the electrons'

kinetic energy is converted to various energy types. The created thermal energy heats the substance, causing it to evaporate and thus sublimate. The melt or the solid can produce vapour if the vacuum levels and temperature are high enough, but a low vacuum level and temperature will affect the vapour formation. As a result, the resulting vapour might be used to coat surfaces (Hossain et al., 2018). To create zinc oxide films, a lot of work has been done utilising the electron beam evaporation process technology. Teimoori et al., (Teimoori et al., 2015) investigated semiconducting ZnO thin films generated by electron beam evaporation for H₂ gas detection. The X-Ray Diffraction (XRD) method was employed to investigate the crystallographic structure of ZnO thin films, while a Field Emission Scanning Electron Microscope (FESEM) was used to investigate the surface shape and chemical composition. A four probe method and a Hall Effect study system were used to measure sample electrical resistivity and carrier concentration. The effect of film thickness on the electrical characteristics and sensitivity of ZnO thin films to H₂ gas at 40 ppm was studied. The results revealed that films with a thickness of 100 nm had the best sensitivity, while increasing thickness decreased sensitivity. For the creation of a ZnO-based thin film for gas sensing, an electron beam evaporation approach was used. As indicated in Table 7, a gas sensor based on ZnO-thin films generated some intriguing results.

Table 7: Electron beam evaporation for growth of ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Reference
ZnO	Thin film	Glass	(Agarwal et al., 2006)
ZnO	Thin film	Glass	(Liu, Yu, & Lai, 2014)
ZnO	Thin film	Sapphire	(Aghamalyan et al., 2003)
Al-ZnO	Thin film	Glass	(Sahu, Lin, & Huang, 2008)
C-ZnO	Thin film	Soda lime	(Akbar et al., 2011)
ZnO	Thin film	Glass	(Mahmood et al., 2010)
ZnO	Thin film	Glass	(Varnamkhasti et al. 2012)
Ag-ZnO	Thin film	Glass	(Kim et al., 2009)
ZnO	Thin film	Quartz	(Choi et al., 2009)
ZnO	Thin	Silicon	(Al Asmar et al., 2005)

2.7 Pulsed laser deposition-As the same name suggests, oilseed laser beam is used in this technique. In the vacuum chamber, pulsed laser beam is directly focused on to the source material. In pulsed laser deposition technique, photon interaction ablates the material which creates a laser plume that is collected on the substrate. Vapor pressure of a target material plays a crucial role in deposition of material on the substrate. Target material and the substrate must have a tiny distance between them. Within 10-15 minutes, high quality samples can be produced (Chrisey & Hubler, 1994).

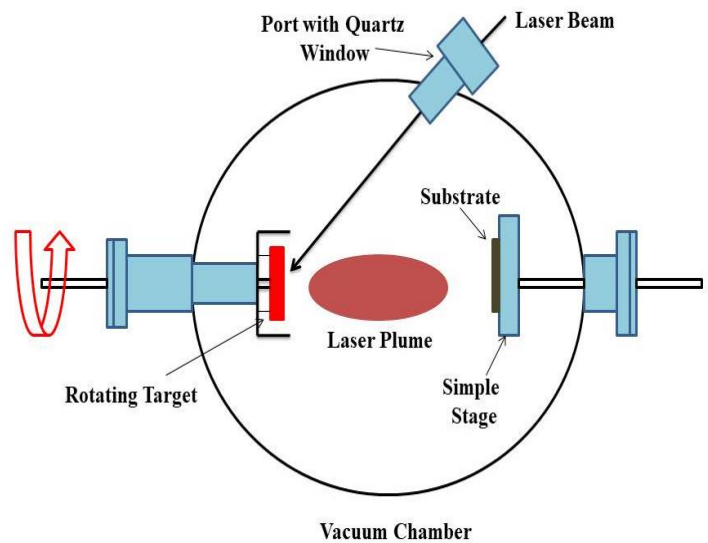


Figure 7: Schematics of Pulsed laser deposition process

A pulsed laser deposition technique was employed to create a ZnO-based thin film for gas sensing after extensive research. A gas sensor based on ZnO-thin films produced some intriguing results, as shown in Table 8.

Table.8 Pulsed laser depositionfor the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Thin film	SiO ₂	Butane	(Mazingue et al., 2005)
ZnO	Thin film	-	NH ₃	(Dikovska et al., 2007)
ZnO	Thin film	Glass	H ₂	(Stamataki et al., 2009)
ZnO	Thin film	Quartz	-	(Kumar et al., 2019)
WO ₃ -ZnO	Thin film	Glass	-	(Ngom et al., 2009)
ZnO	Thin film	Soda lime	-	(Tsoutsouva et al., 2011)
ZnO	Thin film	Glass	LPG	(Al-Assiri et al., 2016)
ZnO	Thin film	GaAs	-	(Shan et al., 2004)
ZnO	Thin film	SiO ₂	H ₂	(Brilis et al., 2005)
ZnO	Thin film	Silicon	NH ₃	(Huotari et al., 2015)

2.8 Sputtering deposition-In this deposition technique, fast ions or particles eject particles from the source material. These ejected particles get deposit on the surface areas of substrate. Here, the ejected atoms which have a wide energy of about 10eV comes out from cathode and moves into the straight path towards anode where cathode is target material and anode is substrate. 1% ejected ions that get sputtered are ionized. By bombardment of other particles possessing higher energy, atoms or molecules of the sample are ejected from the target. This process is known as sputtering. Sputtering has further two types: DC Sputtering, and RF Sputtering There was one more type of sputtering known as diode sputtering which was employed until mid-1970s as diode sputtering incurred higher cost and low deposition. Later on, this technique is used in its new modified version called magnetron sputtering. Magnetron sputtering is a vacuum deposition technique having high deposition rate.

Sputtering technique is much better than vacuum evaporation technique as in sputtering technique sputtered atoms have higher energy which results in better deposition over substrate (Depla, Mahieu, & Greene, 2010).

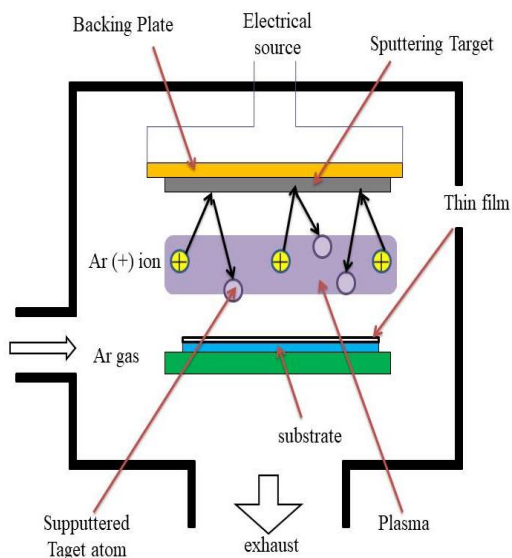


Figure 8: Schematics of sputtering deposition process

2.9 Magnetron sputtering deposition- Magnetron sputtering deposition technique uses plasma for coating and falls under physical vapor deposition technique. Sputtering machine is used in this technique which is filled with inert gas of argon. In the sputtering machine, ions are bombarded towards sputtering material. Argon ions are attracted towards the target material and sputtering atoms are ejected from the material, moving towards the substrate for the deposition only when negative voltage is applied. Plasma as well as energetic sputtered atoms are produced using magnetron sputtering machine. Plasma density on the cathode can be increased by introducing a magnetic field which causes the constraint on the charged particles (Liao et al., 2021) .

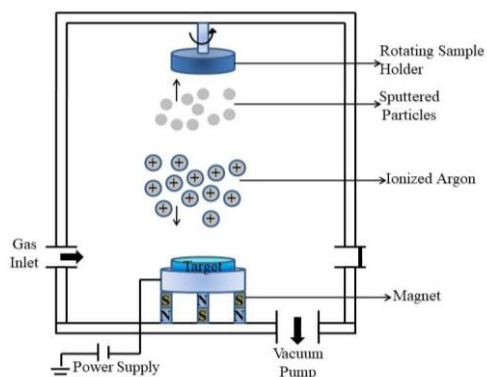


Figure 9: Schematics of magnetron sputtering deposition techniques

There are two types of magnetic sputtering deposition techniques. These are:

1. DC(Direct Current) magnetron sputtering (Hanby et al., 2018)
2. RF(Radio Frequency) magnetron sputtering (Sato et al., 2020)

Magnetron sputtering uses periodic waveform such as asymmetric bi-polar mid frequency pulsed waveforms.

2.10 DC sputtering deposition-For the purpose of bombardment, argon ions are used and on the target material 2-5kV DC voltage is applied along with that a pressure of about 1-10mTorr is applied. Basically, DC sputtering deposition technique is just for the conducting target materials and not for the insulating target materials (Rasheed & Barillé, 2017). This is because on insulating target materials, ions are accumulated over them. Target material act as a cathode towards which argon ions are moved and bombardment takes place due to which target atoms break out from the target materials and sputtering atoms move in a straight path towards the substrate to get deposit on it through which a thin layer forms in a very short period of time (Goh, 2017).

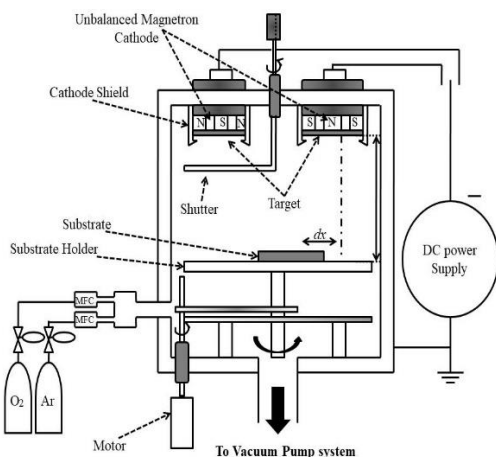


Figure 10: Schematics of DC sputtering deposition process

2.11 RF sputtering deposition - Radio waves are produced by ionized gas atoms in the chamber. This technique uses radio frequency power source. Bombardment takes place in the target material only when ionized gas atoms move towards it and after bombardment, sputtering atoms broke out from the target material which then move straight to the substrate and form a layer over it (Thao et al., 2021). Unlike DC sputtering deposition technique, RF sputtering technique is used for both conducting as well as insulating materials. Frequency of the radio waves is between 0.5-3.0MHz for the ceramic deposition. The whole process takes place during two half cycles of AC power out of which one is negative while the other is positive. When the target material is negatively charged during the first half cycle, ions accelerate towards the target and bombard to split out sputtering atoms. These sputtering atoms remain with the target material until the polarity is changed and when the target material gets positively charged during the second half cycle, sputtering atoms move away from target material towards the substrate to form a thin film over it (Baratto, 2018).

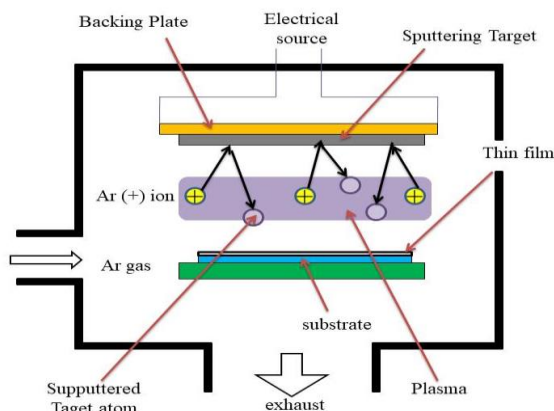


Figure 11: Schematics of RF sputtering deposition process

2.12 Reactive sputtering deposition-In this technique, chemical reaction takes place in which target material reacts with a gas which is mixed with an inert gas to form the sputtering atoms. Inert gas like argon and Reactive gas like oxygen to form oxides, nitrogen to form nitrides, methane or propane to form carbides, etc. are used in this technique. Reactive sputtering deposition technique occurs in vacuum chamber (Iqbal & Mohd-Yasin, 2018). The sputtering atoms produced are then accelerated towards the substrate to form thin film layer. Flat panel display, solar cell and films are fabricated with good optical components due to this technique.(Guillén & Herrero, 2019)

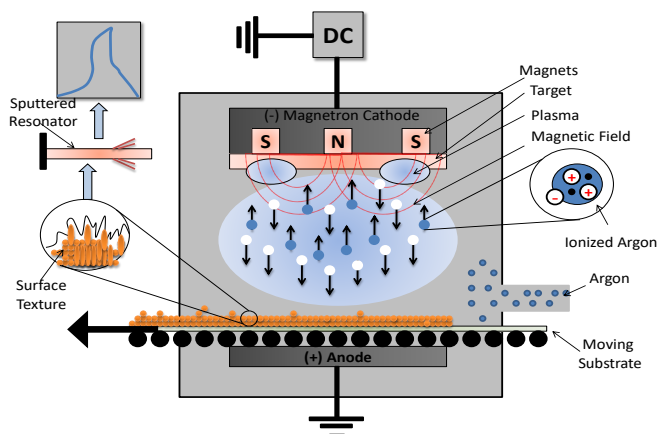


Figure 12: Schematics of Reactive magnetron sputtering deposition process

Another effective method for fabricating ZnO nanostructures on the suitable substrate is sputtering deposition. It is the most favourable technology for the deposition of ZnO nanostructures due to its excellent adherence and homogeneity throughout the substrate. Sputtering works on the principle of atoms being ejected from a source material and deposited on a substrate. The plasma deposition procedure uses argon as the process gas. The RF power, substrate temperature, argon flow, target to substrate distance, and gas pressure all play a role in the sputtering process. Putting an RF magnetron sputtering technique, *Nanotechnology Perceptions* Vol. 20 No.6 (2024)

Ranwa et al.(Ranwet al., 2014) grew vertically aligned ZnO nanorods without using any metal catalyst on the substrate. The growth parameters were set at 500°C, 2×10^{-2} mbar, 60 sccm, 150 W, and 14 cm, respectively, for substrate temperature, chamber pressure, Ar gas flow rate, RF power, and substrate to target distance. RF sputtering, DC sputtering, and magentron sputtering are all options in the sputtering deposition process. All of these approaches are better suited to creating ZnO nanostructures. Some of the top studies linked to the various sputtering processes are listed in table 9.

Table 9: Various sputtering deposition process for the growth of the ZnO based thin film for gas sensing.

Deposition technique	Material	Nano type	Substrate	Target gas	Reference
Rf magnetron sputtering	Y-ZnO	Thin film	Si	NH ₃	(Vinoth et al., 2018)
Magnetron sputtering	ZnO	Thin film	Si	NH ₃	(Y. Zheng et al., 2020)
Rf sputtering	ZnO	Thin film	Glass	NH ₃	(Vinoth et al., 2018)
RF magnetron sputtering	ZnO	Thin film	SiO ₂	NH ₃	(M. Dwivedi et al., 2015)
DC reactive sputtering	ZnO	Thin film	Glass	CO ₂	(Kannan et al., 2014)
DC magnetron sputtering	ZnO	Thin film	Glass	Ethanol	(Hosseinnejad et al., 2016)
DC reactive sputtering	ZnO	Thin film	Si	Humidity	(Kannan et al., 2010)
RF magnetron sputtering	Al-ZnO	Thin film	Si	Ethanol	(Chou et al., 2006)
RF magnetron sputtering	Cu-ZnO	Thin film	Glass	H ₂ S	(Girija et al., 2016)
Sputtering	Cu-ZnO	Thin film	Glass	CO	(Gong et al., 2006)

2.13 Chemical vapor deposition- In this technique, the reactor gas reacts with another gas at a high temperature. Then the gases involved in reaction mixed in the reactor and are deposited on the substrate surface. For example, methane is used as a reactor gas maintained at higher temperature in chemical vapor deposition technique (Manawi et al., 2018). Table 10 summarizes some of the most notable discoveries from the chemical vapour deposition technique for ZnO-thin film gas sensors.

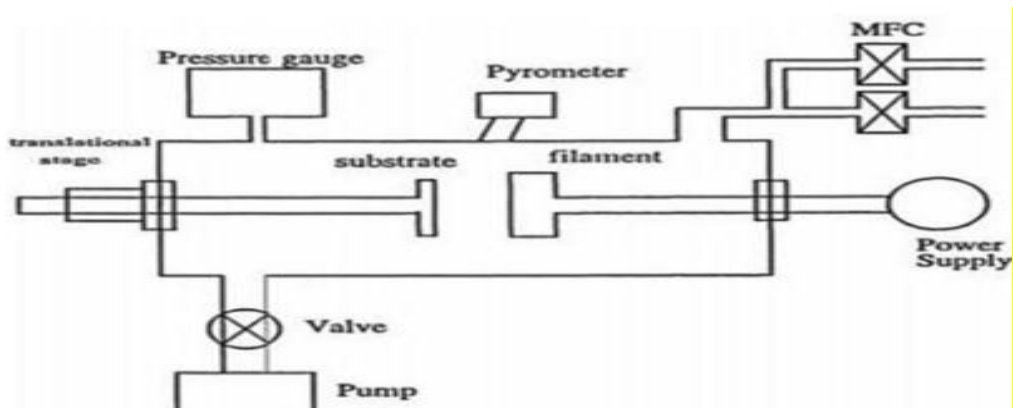


Figure 13: Schematics of chemical vapour deposition process

Table 10: Chemical vapour deposition process for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Nanowires	Glass	CO	(Kiasari et al., 2014)
ZnO	Thin film	Glass	-	(Masuda, 2008)
ZnO	Thin film	Glass	-	(Lu et al., 2007)
ZnO	Thin film	Quartz	Dimethaylamine	(S. Roy & Basu, 2002)
ZnO	Thin film	Glass	Acetone	(Shao et al., 2014)

ZnO	Thin film	Glass	-	(Roro et al., 2008)
ZnO	Nanocactus	Glass	NH ₃	(Ryu et al., 2015)
ZnO	Nanotetrapods	Glass	Ethanol	(K. Zheng et al., 2010)
ZnO	Thin film	Sapphire	-	(Kawaharamura et al., 2008)
ZnO	Nanorods	Glass	O ₃	(Chien et al., 2010)

2.14 Plasma enhanced chemical vapor deposition (PECVD) - Plasma is used in this technique to ionize atoms or molecules. These ionized atoms or molecules deposit on the surface of the substrate to form a thin layer. High frequency waves such as microwave, ultra, high or radio frequency are used to induce plasma (Warner et al., 2013). The frequency range can be from 0-13.56MHz. Microwave frequency such as 2.45GHz is used in electrical power supply in plasma enhanced chemical vapor deposition technique (Teixeira et al., 2011). Table 11, Summarises some of the most important discoveries from the plasma enhanced chemical vapour deposition technique-based ZnO thin films gas sensor.

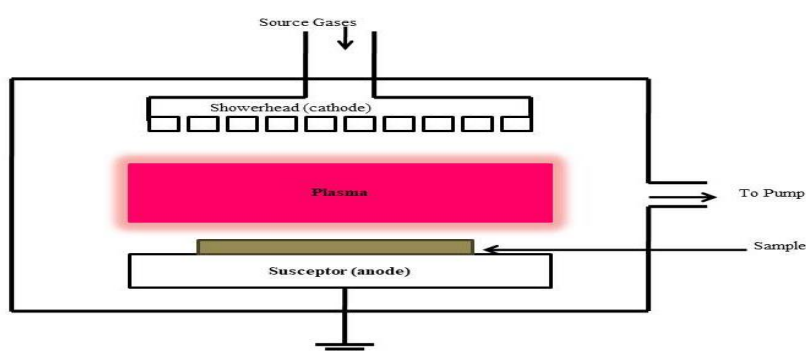


Figure 14: Schematics of PECVD Process

Table 11: PECVD process for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Nanorods	-	Formaldehyde	(N. Han et al., 2010)
ZnO	Nanorods	-	Formaldehyde	(Hu et al., 2012)
ZnO	Thin film	Si	-	(Sanchez-Valencia et al., 2014)
ZnO	Thin film	Si	-	(Chao & Wei, 2015)
ZnO	Thin film	Glass	Antibacterial	(Panigrahi et al., 2011)
ZnO	Thin film	Silicon	-	(Chao & Wei, 2014)
ZnO	Thin film	Al ₂ O ₃	-	(J. Sun et al., 2008)
ZnO	Thin film	Si	-	(B. S. Li et al., 2002)
ZnO	Thin film	Si	-	(Hacini et al., 2021)
ZnO	Thin film	Si	-	(Arif, 2015)

2.15 Atomic layer deposition (ALD)-Gas phase chemical process is utilized in atomic layer deposition. The whole chemical process goes on in sequential manner. First of all, first gas is introduced in the chamber. The first gas forms the first layer known as monolayer over the substrate. Then the second gas is introduced in the chamber to react with the monolayer to form the required thin film over the substrate(Sanctis, Krausmann, Guhl, & Schneider, 2018). ALD was used to create ZnO nanostructured materials with a variety of morphologies, and the gas sensing characteristics and transduction process were investigated. Table 12 summarises some of the most significant findings from the ZnO-thin films gas sensor based on the ALD deposition process.

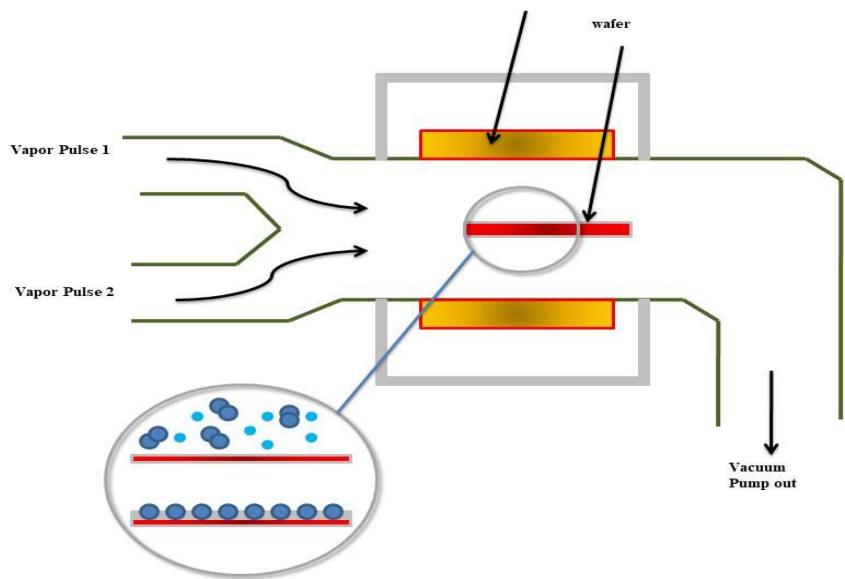


Figure 15: Schematics of Atomic layer deposition technique process

Table 12: ALD process for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Thin film	-	-	(Pung et al., 2008)
ZnO	Thin film	Al ₂ O ₃	CO	(V. A. T. Dam et al. 2010)
ZnO	Thin film	Si	RH	(V. Dam et al., 2011)
ZnO	Thin film	Quartz	C ₂ H ₅ OH	(Naumenko et al., 2013)
ZnO	Thin film	Si	NH ₃	(Hong et al., 2016)
ZnO	Nanorods	Si	NO ₂	(S. Park et al., 2013)
ZnO	Nanowires	Sapphire	NH ₃	(S. Park et al., 2014)
ZnO	Nanorods	Si	H ₂	(S. Park et al., 2014)
ZnO	Fibers	Si	O ₂	(J. Y. Park et al., 2010)
ZnO	Nanorods	p-Si	C ₆ H ₆	(Mirzaei et al., 2016)

2.16 Hydrothermal technique-Hydrothermal synthesis technique is a crystallising and producing nanomaterial directly from solutions by using single heterogeneous phase processes in an aqueous medium at higher temperature and pressure. It is a process which produces oxide powder with a small size distribution at low temperature, avoiding calcination (Zeng et al., 2015). In this technique the temperature is usually between the boiling point of water and critical temperature ($T_c = 374^{\circ}\text{C}$) with a pressure more than 100kPa after a complete process desired product achieved with some impurities. For remove these impurities product will wash with deionized water to remove the impurities. After washed product will drying in air, ceramic nanoparticles with excellent dispersion formed will achieved (K. Sun et al., 2011).

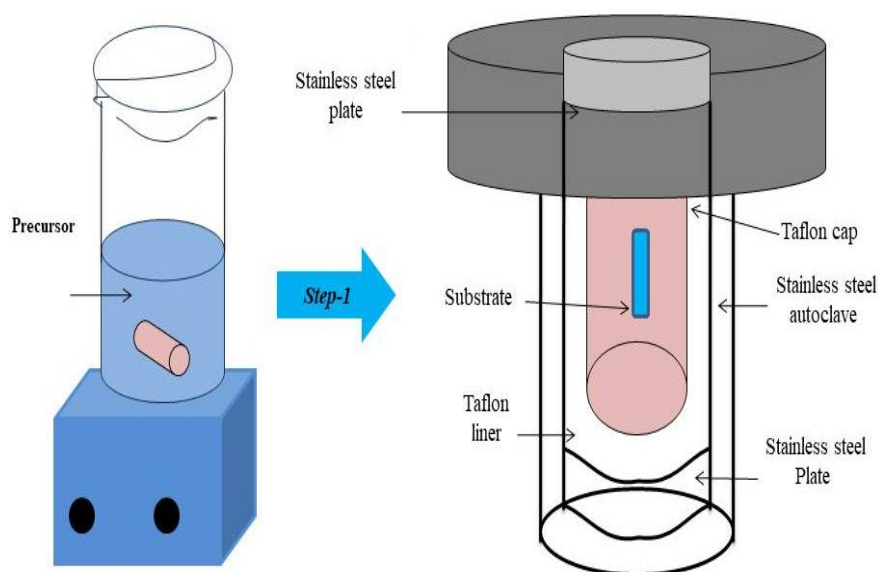


Figure 16: Schematics of Hydrothermal deposition technique process

Another synthesis method for ZnO nanostructures is the hydrothermal process, which involves growing ZnO nanostructures in an autoclave at a lower temperature than other methods. The formation of ZnO nanostructures, on the other hand, takes longer than other approaches. Finally, the growth of nanostructures is triggered by the establishment of a nucleation site. This approach has various advantages, including low temperature growth, low cost, and shapes of nanostructures based on material composition, different pressure, and high crystallinity (Baruah & Dutta, 2009). In Table 13, we summarize a number of studies on hydrothermal-based ZnO thin films.

Table 13: Hydrothermal deposition process for the growth of the ZnO based thin film for gas sensing.

Material	Nano level type	Substrate	Target gas	Reference
ZnO	Thin film	Glass	NO ₂	(V. Patil et al., 2018)
ZnO	Nanowire	Glass	H ₂	(Sinha et al., 2016)
ZnO	Nanorods	Si	H ₂	(J. Wang et al., 2006)
ZnO	Thick film	Alumina	VOCs	(Bai et al., 2010)
ZnO	Nanorods	Glass	LPG	(Gurav et al., 2014)
ZnO	Nanorods	Glass	NO ₂	(Jagdale et al., 2018)
ZnO	Microtube	Si	CO	(J. X. Wang et al., 2007)
Co-ZnO	Nanorods	FTO Glass	NO ₂	(Zou et al., 2015)
ZnO	Core-shell	SiO ₂	H ₂	(Tsai et al., 2019)
CeO ₂ -ZnO	Thick film	Alumina	Ethanol	(Rajgure et al., 2014)

There are numerous ways available for creating ZnO-based nanostructured. Each approach has its own specialty. Table 14 summarises the Advantages, Disadvantages and applications of each approach.

Technique	Advantages	Disadvantages	Application	Reference
Spray Pyrolysis	<ul style="list-style-type: none"> ➤ It is both cost-effective and simple to carry out. ➤ Coating can be done on surfaces with complicated geometries ➤ It produces a thin layer that is relatively uniform and of high quality. ➤ Dopant could be easily added. 	<ul style="list-style-type: none"> ➤ With a greater grain size, there is less consistency in the film. ➤ Low rate of deposition. ➤ Solution squandered 	<ul style="list-style-type: none"> ➤ It employed in gas sensor, solar cell, and solid oxide fuel cell applications. 	(Kozhukharov & Tchaoushev, 2013; Leng et al., 2019)
Sol-gel	<ul style="list-style-type: none"> ➤ It operates at low temperatures. ➤ It has the ability to produce extremely fine particles. ➤ Energy consumption is reduced. 	<ul style="list-style-type: none"> ➤ The cost of the precursor materials may be too expensive. ➤ its sensitivity to moisture ➤ During drying, moist gel shrinks and cracks. 	<ul style="list-style-type: none"> ➤ It's employed in a variety of applications, including protective coatings, catalysts, piezoelectric devices, and insulating materials. 	(Attia, 2012; Pierre, 2020)
Spin coating	<ul style="list-style-type: none"> ➤ The thickness of a thin film can be easily changed. ➤ Consistent thin film produced at a minimal cost. ➤ It results in less material loss. 	<ul style="list-style-type: none"> ➤ The material efficiency is really low. ➤ Produces several layers of deposition. 	<ul style="list-style-type: none"> ➤ It can be found in electronic semiconductors, spectroscopic gas sensors, and other applications. 	(Kaviyarasu et al., 2017; Tyona, 2013)
Dip coating	<ul style="list-style-type: none"> ➤ It is inexpensive. ➤ It is simple to control the thickness. ➤ It have ability to cover the entire surface of the substrate 	<ul style="list-style-type: none"> ➤ The thickness of the layer varies over the entire substrate. ➤ On the bottom of pieces, fatty margins form. ➤ It's a slow and arduous procedure. 	<ul style="list-style-type: none"> ➤ It's employed in the production of bulk items including coated textiles and filters. 	(Ceratti, Louis, Paquez, Faustini, & Grosso, 2015; Tang & Yan, 2017)
Hydrothermal technique	<ul style="list-style-type: none"> ➤ It is appropriate for large, high-quality crystal. ➤ It's simple to control the product's morphology. ➤ It created good crystallinity ions. 	<ul style="list-style-type: none"> ➤ The cost of an autoclave is high. ➤ operates at a high temperature ➤ Concerns about safety 	<ul style="list-style-type: none"> ➤ It's employed in develop Nano crystals, gas sensor applications, and research labs. 	(A. Han, Zhang, Li, Wang, & Li, 2020; Suchanek & Riman, 2006)
Vacuum evaporation	<ul style="list-style-type: none"> ➤ Films is extremely pristine and of exceptional quality. ➤ The film's growth method is rather straightforward. ➤ It is simple equipment that is straightforward to use. 	<ul style="list-style-type: none"> ➤ It's possible that the amount of source material used isn't very high. ➤ Many chemicals and alloy combinations are just difficult to deposit. ➤ Without correct fixturing and movement, there is a lack of homogeneity in film thickness over wide areas. 	<ul style="list-style-type: none"> ➤ It is used in Optical interference coatings, decorative coatings, permeation barrier films materials, and electrically conducting films. 	(Asatekin et al., 2010; Jamkhande, Ghule, Bamer, & Kalaskar, 2019)
Pulsed laser deposition	<ul style="list-style-type: none"> ➤ Multi-component film is readily available. ➤ It has a high rate of deposition. 	<ul style="list-style-type: none"> ➤ Its deposition is sluggish on average. ➤ It has a patchy coverage. 	<ul style="list-style-type: none"> ➤ Solar cells, optical industries, and microelectronics all employ it. 	(Boyd, 1994; Morintale, Constantinescu, & Dinescu, 2010)

	<ul style="list-style-type: none"> ➤ It's simple to clean and can make a wide range of thin film materials. 			
Sputtering deposition	<ul style="list-style-type: none"> ➤ It can deposit metals, insulators, alloys, and composites. ➤ Uniform thickness over vast substrates, big area targets might be used. ➤ Deposition control that is more repeatable 	<ul style="list-style-type: none"> ➤ Some materials have a slow deposition rate. ➤ Ion bombardment has caused damage to the substrate. ➤ Ionic bombardment causes some materials (such as organics) to deteriorate. 	<ul style="list-style-type: none"> ➤ Integrated circuits, coating on glass, microelectronics all employ it. 	(Abegunde, Akinlabi, Oladijo, Akinlabi, & Ude, 2019; Baptista, Silva, Porteiro, Míguez, & Pinto, 2018)
Chemical vapor deposition	<ul style="list-style-type: none"> ➤ It can be used in Ceramics, glass, metals, and metal alloys are among the foundation materials. ➤ High purity ➤ Due to its excellent adhesion qualities, it stays connected in high-stress settings and when the surface flexes. 	<ul style="list-style-type: none"> ➤ Surface that is difficult to mask. ➤ Size is restricted by the capacity of the reaction chamber. ➤ In most cases, it's used at greater temperatures. 	<ul style="list-style-type: none"> ➤ It is used in integrated circuits, conductors, fiber optics, passivation layer, sensor etc. 	(Heydari Gharahcheshmeh & Gleason, 2019; Manawi et al., 2018)
Atomic layer deposition	<ul style="list-style-type: none"> ➤ Its ultra-thin, high-quality films. ➤ Processing at a low temperature. ➤ The ALD mechanism's self-assembled nature. 	<ul style="list-style-type: none"> ➤ It has a high rate of material waste. ➤ The viability of the economic. ➤ the time it will take for chemical reactions to occur. 	<ul style="list-style-type: none"> ➤ It used in Li-ion batteries, micro-electro mechanical conformal, and nano coating films, fuel cells etc. 	(Oviroh, Akbarzadeh, Pan, Coetzee, & Jen, 2019; Weber, Julbe, Ayrál, Miele, & Bechelany, 2018)

3. Conclusion

Several deposition processes were used to successfully manufacture ZnO thin films. To characterise and examine the produced thin films, several technologies such as XRD, SEM, FESEM, AFM, EDX, and UV-Vis spectrophotometer were used. Film thickness, surface morphology, electrical characteristics, and optical properties of produced ZnO thin films are all related to the deposition procedure used in this work. The exceptional quality of ZnO film has grabbed academic interest, and their manufacturing methods have already provided some research results. As new fields of application emerge, the technology for making them is projected to advance significantly, allowing ZnO films with more consistent performance to become more industrialised.

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