© December 2021| IJIRT | Volume 8 Issue 7 | ISSN: 2349-6002

A Review: ZnO – From Synthesis to Application

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***Abstract* - Many efforts are taken on oxide nanostructures over the last twenty years thanks for large number of applications. ZnO thin film is one among the II-VI compound semiconductors and it is composed of hexagonal wurtzite crystal structure. ZnO based nanostructures have gained remarkable attention worldwide for the sensing, photo sensing, behaviour as a semiconductor metal oxide in several industries. The main motivation of this thematic review is to research the various deposition techniques of pure and doped oxide nanostructures, and their application in sensing field. This review summarizes the various deposition techniques and main chemical route utilized in the sol-gel synthesis of ZnO thin film and highlights the study of various characterizations. Finally, a large range of uses of ZnO nanostructures in various applications in photo sensing, gas sensing, humidity sensing, and glucose sensor are highlighted during this article.**

***Index Terms* - Zinc Oxide, Nanostructure, Thin film, Sol-gel method, Dopants, sensing, etc.**

1.INTRODUCTION

Nanotechnology is a sophisticated technology, which deals with the synthesis of nanoparticles, processing of the nano materials and their applications. Nanomaterials will be defined as those materials, which have size but 100 nm a minimum of in one dimension. Nano materials are of typically tremendous interest. Thanks to their noticeable performance in electronics, optics and photonics. Nano materials were classified as zero dimensional, one dimensional, two dimensional, three-dimensional nanostructures. Zero dimensional nanostructures are like nanoparticles [1] or quantum dots, are widely employed in photovoltaic cell [2]. One-dimensional nanostructures like nano wires, nano rods, nano tubes are employed in research also as industrial application [3]. Two-dimensional nano materials like thin films are widely employed in optical coatings.

As we know, the skinny film could be a layer of fabric starting from fraction of nanometer to many micrometers in thickness. Thin films are crystalline or amorphous layers, deposited on a substrate. Thin film technology could be a self-organizing structural evolution. The study of thin film phenomena has been accustomed a big extends over the last four decades. Miniaturization criteria made the utilization of thin films practically necessary. Thin film technology is pervasive in many applications including microelectronics, optics, magnetic, micro mechanics, high resistant coating, etc. This technology involves synthesis of individual molecules or atoms. The synthesis of metal oxides nanostructures have stimulated the good interest due to their novel properties which give intense research efforts to fabricate the efficient miniaturized devices for the various applications in Nano-electronics and photonics. Generally, transition metal oxides are used for skinny film synthesis like TiO_2[4], SnO_2[5], ZnO [6,7], WO_3[8,9], ZrO_2[10], etc.

Out of that, ZnO is a semiconductor material with a wide band gap energy (~3.4 eV) and large binding energy (60meV) at room temperature [11]. ZnO crystallizes in two main forms, hexagonal wurtzite, and cubic zinc blend. Under ambient conditions, it exhibits a hexagonal wurtzite structure [12, 13, 14]. This enables some applications in optoelectronic such as light emitting diode, laser diodes, and photo detectors. ZnO possesses large piezoelectric and pyroelectric properties. These makes ZnO generally used for sensors, transducers [15], and actuators [16].

2. ZINC OXIDE THIN FILM DEPOSITION

The synthesis of metal oxides nanostructures have stimulated the nice interest thanks to their novel properties which give intense research efforts to fabricate the efficient miniaturized devices for the applying in various Nanoelectronics and photonics. The technique are used depends upon the fabric of interest, kind of nanomaterial viz. zero dimensional (0-D), one-dimensional (1-D) or two-dimensional (2-D), their sizes and quantity.

2.1 Different methods

There are various approaches for the synthesis of ZnO nanostructures. A number of the already existing conventional techniques to synthesize differing types of materials are optimizing to induce novel nanomaterials and a few new techniques are developed. an outline on several deposition methods like physical vapour deposition (PVD), chemical vapour deposition (CVD), dip coating, spin coating, screen printing, spray pyrolysis and sol-gel method for ZnO thin films are discussed during this review.

2.1.1 Physical vapour deposition (PVD)

Physical vapour deposition is low coating processes within which the coating is produces by a physical process. There are two main types: Evaporation and sputtering. In both cases, the source material may be a solid. A reactive has could also be employed in the deposition chamber to deposit compound coatings from an elemental source. It should accustomed maintain the stoichiometry of coatings from compound sources, though thinner layers are utilized in microelectronics and thicker layers are used for top temperature [17, 18].

The advantages of PVD are excellent process control, low deposition temperature, dense and adherent coatings, and elemental, alloy and compound coatings is feasible. But it's some disadvantages like Vacuum processes with high cost of capital, limited component size treatable, relatively low coating rates, poor throwing without manipulation of components.

2.1.2 Chemical vapour deposition (CVD)

Chemical vapour deposition (CVD) may be a widely used materials processing technology within which thin films are formed on a heated substrate via a reaction of gas-phase precursors. This is often a robust technology for producing high-quality solid thin films and coatings. The deposition temperature is usually within the range of 800 – 1000°. During this process the thickness is restricted to about 10μm because of the thermal expansion mismatch stresses, which develop on cooling, which also restrict the coating sharp edges components [19, 20]

There are different advantages of CVD are high coating hardness, good adhesion, and good throwing power. Additionally, some disadvantages for this CVD method as hot temperature process, sharp edge coating is difficult, limited range of materials may be coated and environmental concerns about process gases [21].

2.1.3 Dip coating

Dip coating could be a simple and effective technique, which is usually utilized in manufacturing across a large range of various industries. Within research and development, it has become a very important coating method for the fabrication of thin films employing a Purpose-built dip coater. When the method is optimized, dip coating may be accustomed produce uniform films. Importantly, key factors like film thickness will be easily controlled [22].

One advantage of dip coating over other processing techniques is that the simplicity of its design. It's low cost to setup and maintain and might produce films with extremely high uniformity and a roughness of nanometres [23, 24].

2.1.4 Spin coating

Spin coating may be a procedure wont to apply uniform thin films to flat substrate. A coating may be a covering that is applied to the surface of a substrate. A machine used for spin coating is named a spin coater. A typical process involves depositing a little puddle of a fluid resin onto the centre of a substrate and so spinning the substrate at high speed. This is often widely utilized in micro-fabrication, where it is wont to create thin films with thickness below 10nm. One in every of the foremost important factors in spin coating is repeatability and spin speed [25, 26].

The speed of substrate affects the degree of radial force applied to liquid likewise because the velocity and characteristic turbulence of air immediately above it. The high-speed spin step generally defines the ultimate film thickness.

2.1.5 Spray pyrolysis

Spray pyrolysis has been applied to deposit a good type of thin films. These films were employed in various devices like solar cells, sensors, etc. This is often a processing technique being considered in research to organize thin and thick films, ceramic coatings, and powders. It represents a simple and comparatively cost-effective processing method. It offers a very easy technique for preparing films of any composition [27, 28].

Even multilayer films are often easily prepared using this system. Here is a few disadvantages because it isn't easy to rescale and there are difficulties with determining the expansion temperature [29,30].

2.2 Sol-gel method in details

Among these methods, the sol-gel technique is most engaging method for ZnO nanostructure synthesis due to its low cost, high reliability, good repeatability, simplicity of process, low process temperature, simple control of physical characteristics and morphology of nanoparticles, good compositional homogeneity, and optical yet sensing properties.

Sol-gel is wet chemical technique that is extensively used for the event of nanomaterials. Because the name suggests sol-gel involves two sorts of materials or components, 'sol' and 'gel'. Sol gels are known since the time when M. Ebelman synthesized them in 1845. Very first thing is that everyone sol-gel formation process is typically a coffee temperature process. During this chemical procedure, the answer gradually converts into a gel like diphasic system, which contains both liquid phase and solid phase. The sol-gel procedure consists of various steps as hydrolysis, condensation, aging, drying, calcination, and warmth treatment [31, 32, 33].

- Sol formation:

A sol may be a colloidal or molecular suspension of solid particles of ions in a very solvent. Hydrolysis of metal organic reactant in an organic solvent that is miscible with water or inorganic salts in water leads to formation of sol.

M-O-R + H_2O → M-OH + R-OH

- Gel formation:

A gel may be a semi-rigid mass that forms when the solvent from the sol begins to evaporate and also the particles or ions left behind begin to affix together in an exceedingly continues network. Condensation followed by polycondensation of sol ends up in the formation of the gel.

Water condensation:

Hydrolyzed species condense releasing water.

M-O-R +HO-M → M-O-M +H_2O

Alcohol condensation:

Hydrolyzed species condense with unhydrolyzed species releasing alcohol.

M-O-R +HO-M → M-O-M +R-OH

Aging of gel during which polycondensation reaction occurs, can exceed 7 days is critical to the prevention of cracks in gels that are cast.

- Aging:

During this process, polycondensation continues. Additionally, it changes to the structure, properties, and porosity. During aging, the porosity decreases, and also the distance between the colloidal particles increases.

- Drying:

After the aging process, drying takes place. It's nothing but removal of pour liquid. Under hypercritical conditions, upon drying, the network does not collapse and therefore the aerogels are formed. Under ambient conditions, upon thermal evaporation, shrinking of pores occurs and the xerogels are formed.

- Calcination:

Lastly, calcination is performed to attain nanoparticles. During calcination, xerogels is heated to 800°C. The pores of gel network are collapsed and remaining organic species are volatilized. The surface bound M-OH groups are removed, there by stabilized the gel against rehydration. Calcination leads to densification and decomposition of the gel.

- Heat treatment:

By heat treatment, the material is shaped into desired form such as films, fibers and nano sized powder. Subsequently it can be converted into ceramic material.

In sol-gel technique, there are different factors, which affect the final product they are as precursor nature, hydrolysis rate, aging time, pH, molar ratio between H_2O and precursor, calcination Time [34, 35, 36, 37].

Advantages of sol-gel method:

- Mono sized nano particles are produced by this method.
- It is beneficial for the synthesis of glasses, glass ceramic or ceramic materials at lower temperature.
- It can produce thin bond coating to produce excellent adhesion between the metallic substrate and also the top coat.
- It can produce thick coating to produce corrosion protection performance.

- This method can have cold sintering capability usually 200-600°C.
- It can get inorganic- organic composites.
- This can coat onto large area or complex shape objects.
- It can get fibres.
- This has high uniformity, multi component system.

3. DIFFERENT DOPANTS ELEMENT

The addition of very bit of an overseas substance to a very pure substance is thought as doping. The addition of those impurities serves different purposes under different needs. Doping is that the primary methods of controlling semiconductor properties like the band gap, electrical conductivity, and ferromagnetism. Because the band gap is so small for semiconductor, doping with touch of impurities can dramatically increase the conductivity of the fabric. When approximately 1 dopants atom is added per 100 million atoms, the doping is alleged to be low or light. When more dopants atoms are added, approximately one per ten thousand atoms, the doping is referred as high or heavy.

Many metals and non-metals are successfully accustomed dope ZnO nanostructures by various deposition methods. ZnO nanostructure metal doping includes Co [38], Ni [39], Al [40], Fe [41], Ga [42, 43], Eu [44] and Cu [45]. Similarly, non-metal doping includes Cl [46], C [47] and P [48].

The optical measurement results confirm that each one the ZnO thin films had high transmittance within the visible region 0.5 wt%. Co-doped ZnO thin film had the very best transmission and the strongest ultraviolet emission [49]. The absorption fringe of ZnO observed to be less than Ni-ZnO, and the optical band gap of undoped ZnO thin film decreases slightly from 3.28eV to 3.20eV of 10% Ni-doped ZnO thin film [50]. The Fe-doped ZnO nanorods showed temperature ferromagnetic magnetization vs. field hysteresis and magnetic increases [51]. When copper doped to ZnO, it can enhance photocatalytic activity of a ZnO thin film [52].

4. CHARACTERIZATION OF ZNO NANOMATERIAL

Under general conditions, ZnO is single crystalline and exhibits a hexagonal wurtzite structure. The structure of ZnO nanowires might be revealed by X-ray diffraction (XRD) and scanning microscopy (SEM). Both XRD and SEM demonstrate the hexagonal wurtzite structure of the ZnO nanowires [53, 54]. For wurtzite structure, the lattice parameter a and b are equal and is within the range 3.2475 to 3.5201A° and c is within the range 5.2042 to 5.2075 A°. The bond between Zn and o within the Bravais lattice possesses very strong ionic character [55].

Further structural characterizations may be dole out by transmission microscopy (TEM). A low-resolution TEM image of ZnO nanowires with a homogeneous diameter size that does not vary significantly along the wire length [56]. After we doped some material in ZnO, the optical band gap decreases with increases in dopants concentration [57, 58]. Additionally, after doping, from the EDX spectra, XPS spectra and XRD pattern, there was not the other secondary phase of dopants or its oxide that has been observed [59]. Two oxidation number states of dopants were identified in ZnO thin film by X ray photoelectron spectroscopy (XPS)[60].

In ZnO crystal, the underside of the conduction band is thanks to occupied 2p states of O^{2-} and the top of the valence band is because of the empty 4s states of Zn^{2+}. The valence band further splits into three-sub valence band under the influence of spin.

5. APPLICATIONS OF ZNO THIN FILMS

5.1 Photo sensor

The large band gap of ZnO and high excitation energy makes it should ideal material for blue, and UV LED, ZnO is widely available and cheap, so it is an advantages over other material from the value point of view. The limiting think about realizing ZnO based LED was the dearth of stable and reproducible p-type ZnO [61, 62]. Various ZnO based hetero-junction LED in UV and visual range has been reported as yet. Earlier it had been difficult to attain p-type doping in ZnO but nowadays, several researchers have reported p-type ZnO, and heterojunction LED supported it. Some people fabricated As-doped ZnO and demonstrated LED and a few fabricated Sapphire LED by RF sputtering method [63, 64]

For short-wavelength semiconductor LASER diodes, wide band gap materials are ideal [65]. Nowadays blue and UV LASER is supported GaN materials [66]. However, due to the massive exciton separation energy of 60 meV as compared thereto of 25 meV of GaN, ZnO will be a more brilliant material for UV and blue LASER application. The lasing phenomenon in ZnO occurs because of exciton-exciton scattering. Various researchers have observed stimulated emission from ZnO.

5.2 Humidity sensor

ZnO as a sensitive material shows poor linearity and low sensitivity for ratio detection, which limits its application as a humidity sensor. With the in-depth research requiring the sensitivity of the humidity sensor, the linearity stability has to be further improved. to boost the responsiveness of ZnO humidity sensors, metallic element doping (Au, Ag, Pd and Pt) could be a frequently used method [67, 68]. Silver (Ag) is one in all the foremost conductive materials and its low cost and good catalytic performance are widely utilized in sensors.

The introduction of modified silver nanoparticles into ZnO can control the surface morphology and crystal structure of ZnO, which is anticipated to boost the performance of humidity sensors. Moreover, after Ag is introduced into ZnO, the adsorption sites on the surface of the fabric will increase, and therefore the number of surface defects will increase [69]. On the one hand, large adsorption sites and high surface defects can wee-wee molecules adsorbed on surface of the fabric decompose quickly, and hence improves the response speed of the sensor. On the opposite hand, silver particles have good electrical conductivity, which is useful to boost linearity of the sensor, so Ag/ZnO stuff can provide a brand new idea for the preparation of high-performance humidity sensors [70,71].

5.3 Gas sensor

ZnO is one of the earliest discovered and most generally used oxide gas sensing materials. Gas sensors have many important applications like environmental pollution control, fire detection, alcohol breath analyzer, process controller in industries, detection of harmful gas leaks in mines and industries [72]. Semiconducting oxide-based gas sensors are easy to fabricate, have low cost and their surfaces have good sensitivity to the adsorbed gasses [73]. Permanently sensitivity, the film surface should have higher grain density with the porous surface [74]. ZnO being physically and chemically stable may be a decent choice for thin-film gas sensor. Doping ZnO with suitable elements inappropriate amount increases the surface density of grains and porosity thereby improving the sensing selectivity and latency of the film [75].

There are some reported works like Pd-doped ZnO gas sensors for H_2 detection by Al-Zaidi et al. [76], ZnO thin film gas sensor by RF sputtering for H_2, NO_2, and hydrocarbon detection by Sadek et al. [77] etc. Balakrishnan et al. [78] reported the detection of NH_3 gas by p-type ZnO thin film.

5.4 Bio sensor

The biosensor may be a transducer that detects the biological response and converts it into constant electrical signal. Biosensors have many important applications especially within the field of health care and food-processing industries. They are used for chemical and biological analysis. They are also used for clinical analysis and environmental monitoring. The materials to be used for biosensor should be biocompatible and non-toxic so the biological activity of the element to be recognized is retained.

ZnO because of its biocompatibility, non-toxicity and therefore the antibacterial property could be a good selection for biosensors. ZnO contains a high isoelectric point (9.5) therefore; elements with an occasional isoelectric point may be immobilized there on through electrostatic interaction. ZnO nanostructures as biosensors are often wont to detects elements like for H_2O_2, urea, protein, glucose, human IgG, DNA (PAT gene), Phenol, catechol, cholesterol, etc. [79, 80].

6. CONCLUSION

ZnO has emerged as a vital semiconductor material due to its excellent electrical, optical, piezoelectric, and gas sensing properties. Even, lot of works on ZnO nanostructure thin films in terms of their synthesis similarly as applications have already been done and reported in literature but there are still many avenues, which deserve exploration to realize a far better understanding of ZnO nanostructures systems. By synthesis point of view of ZnO thin films, deposition is extremely important for the fabrication of various nanodevices. Therefore, Synthesis, characterization and applications of ZnO thin film is one among the promising directions.

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