



ZnO THIN FILMS BY SOLGEL METHOD: A REVIEW

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ABSTRACT

Researchers are working on extensive use of different oxide materials thin films from last few decades. In this review article, different deposition methods of preparation of ZnO thin films by various researchers are studied. Out of which, Sol gel method is found most suitable, simple, low cost method, hence studied and explained here in detail. During the last years, ZnO thin films have been studied extensively due to their potential applications in applications as optoelectronic devices or photovoltaic cells, gas sensing device, humidity sensing device, piezoelectric transducers, optical waveguides, acousto-optic media, surface acoustic wave devices, transparent conductive electrodes, solar cell windows, varistors etc. Effect of doping on physical properties of ZnO and their use in different sensing applications are studied and mentioned here.

Key words: Thin film, ZnO, Sol gel method, sensing applications, dopants etc.

I. INTRODUCTION

Many hands are working to make the life of human being more and more sophisticated. Different industries, which are producing solid state devices, are totally dependent on the formation of thin solid films of a variety of materials by deposition from the gas, vapor, liquid, or solid phase. Electronic engineers have continuously demanded films of improved quality and sophistication for solid-state devices, requiring a rapid evolution of deposition technology. Different researchers are engaged from long back, to understand the physics and chemistry of different materials, synthesis of different materials and different thin film or thick film deposition techniques. Scientists from all corners of the worlds are busy to find use of thin films prepared by various methods for different applications like solar cell, biosensors, photo sensors, gas sensors, humidity sensors, tips of cutting tools etc.

Thin film deposition needs a clean substrate – the base material to deposit the film on, need a source for the film material, needs to bring somehow the source material in contact with the substrate and have to stick it and if certain pattern of film is necessary then etching of the film as per requirement.

Various oxide materials available on the earth in abundant, are found to be useful in different sensing devices. SnO₂, ZnO, WO₃, TiO₂, Fe₂O₃, Cr₂O₃, CeO₂, ZrO₂, and CeO₂-ZrO₂, Al₂O₃, Y₂O₃ composites are the most popular oxide materials used for various sensor applications.

Zinc oxide (ZnO) is found to be most important material for various applications. In this article we review different research papers related ZnO and we found that thin films of ZnO can be prepared by various methods and used in many different sensor applications. Doping of pure ZnO thin films is found to show enhanced characteristics in various sensors.

II. ZnO IS A PROMISING SEMICONDUCTOR FOR DIFFERENT SENSOR APPLICATIONS

Zinc oxide (ZnO) is a type II-VI semiconductor with a direct band gap of 3.37 eV and stable Wurtzite type structure with lattice parameters $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$ [1].

From the last few years, ZnO thin films have been studied extensively due to their potential applications as optoelectronic devices or photovoltaic cells, conductive gas sensors, piezoelectric transducers, optical waveguides, acousto-optic media, surface acoustic wave devices, transparent conductive electrodes, solar cell windows and varistors [2–8].

ZnO is recognized as a promising candidate for blue and ultraviolet light-emitting diodes or laser diodes because of its wide-band gap of 3.37 eV and large excitation binding energy of 60 MeV [3–8]. It is an important semiconductor material due to its applications, which include transparent conductive oxides (TCO) [9, 10], ultraviolet (UV) blockers, and photo catalysts, among others. It can also be used as biosensor applications [11].

Due to their excellent properties such as optical, electrical, high chemical and mechanical stability, and its abundance in nature, the zinc oxide (ZnO) thin films, have a low cost compared to the most material currently used transparent conductive oxide materials. The structural, optical and electrical properties of ZnO thin films were governed by synthesis parameters, deposition conditions and dopants.

III. VARIOUS METHOD TO PREPARE ZnO THIN FILMS

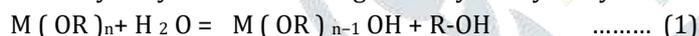
ZnO thin films have been prepared by various techniques such as sputtering [12], magnetron sputtering [13], chemical vapour deposition (CVD) [14], metal organic chemical vapour deposition (MOCVD) [15], pulsed laser deposition (PLD) [16], hydrothermal [17] and sol-gel process [18–21], co-precipitation method [22], chemical spray pyrolysis [23], physical vapour deposition [24], Chemical bath deposition method [25], ultrasonic spray pyrolysis technique [26], Cathodic magnetron sputtering and reactive electron beam evaporation [27–31], electrodeposition [32, 33].

Of all those synthesis techniques, the sol-gel technology is one of the most promising method to produce ZnO colloids [35–46] and to prepare ZnO nanostructured films due to its simplicity, safety, low cost and highly controlled way. [18-21,34, 47-54].

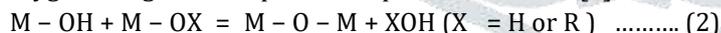
IV. DETAILS OF SOLGEL METHOD

Sol gel processing is a well – recognized, cost competitive, bottom up synthesis technique, which is used in the field of material science and ceramic engineering for the generation of oxide nanopowder and composite nano powders form a sol followed by gel formation [18-21, 55-66]. The sol gel process have number of applications in many areas, such as optics, electronics, ionics, mechanics, energy, environment, biology, medicine. Since 1980, sol – gel technology has been successfully applied in glass, oxide coatings and functional ceramic powders, especially composite oxide such as high critical temperature superconducting oxide material synthesis which is difficult to prepare by traditional method. Sol gel processes are mainly based on hydrolysis and condensation reactions of metal alkoxides, the molecular precursor that develop an oxide network in a liquid medium [55-57]. The structures of oxide materials change from nanoparticles to gel according to the reaction rate and the subsequent drying and post treatment [56, 57-59].

According to the types of precursors, the sol-gel process can be divided into two types: organic and inorganic. The organic route is that the sol-gel is prepared by metal alkoxides which can be considered as a two-step inorganic polymerization. The first step is the hydrolysis of alkoxide ligands to yield hydroxylated metal centers [60]



The second step is the condensation of the hydroxylated species to form oxypolymers, involving an oxylation reaction which creates oxygen bridges and expels XOH species as follows [7]:



Advantages and shortages of sol-gel processing

The sol-gel process provides samples with high purity, homogeneity, and structure of easy control. The most important advantages of the sol-gel process in the preparation of functional materials are as follows:

1. In all stages, the temperatures required are low and close to room temperature. Then, thermal decomposition of organic material and any entrapped species is minimized leading to high purity and stoichiometry [56].
2. As the organometallic precursors for different metals are miscible, the homogeneous sol solutions are easily achieved [56]. Since the sol-gel is initiated by the reaction of the solution, the materials are very uniform and easy to modify, which is crucial for controlling the physical and chemical properties of the material.
3. Precursors such as metal alkoxides and mixed alkyl/alkoxides are easily purified by common techniques (e.g., distillation or sublimation), which lead to high-purity products [56].
4. The chemical conditions are mild in sol-gel process. Hydrolysis and condensation are catalyzed by acid or alkali under mild pH conditions [56, 62, 63].
5. Highly porous and nanocrystalline materials can be synthesized by this method [56].
6. Colloid particle size and pore size, porosity, and chemistry of the final product can be optimized by chemical treatment of the precursors, controlled rates of hydrolysis, and by condensation [2].
7. Incorporating several components in a single step or in two steps [56].
8. Production of samples in different physical forms [56, 64]. Starting from the same raw material, changing the process can get different products, such as fiber, powder, or film and composite materials.

9. Treating temperature is low, the inorganic materials can be synthesized under the condition of low temperature at about 600°C, the composition and the structure of the product are uniform, the grain size is small, the activity of the material particles is increased, and the performance of the material is expanded.
10. Suitable for large-scale industrial production. The negative factors of sol-gel processing include high precursor cost, overall high cost, and environmental problems associated with the disposal of large quantities of organic by-products. A common theme out of the negative comments was wet chemical processing using alkoxides as precursors [65]. The sol-gel process is more complex in terms of the difficulty in phase control, which is the different chemical and crystal morphology formation at different temperatures. The morphology is relatively simple, generally, spherical particles. Gelation, drying, and heat treatment take a lot of time to prepare the sample. In the stage of drying and heat treatment, the sample has a great weight loss and residual stress, film prone to cracking and objectively restricting the thickness of thin film and result in film residual porosity.

V. ENHANCEMENT OF PHYSICAL PROPERTIES OF ZnO FILMS BY VARIOUS DOPANTS: USEFUL IN DIFFERENT SENSING APPLICATIONS

Doping ZnO with selective elements has become an important route for enhancing and controlling its optical, electrical, and magnetic performance, which is usually crucial for their practical applications in various sensor applications [67].

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