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Influence of pH on ZnO and TiO_2 Nanomaterials Synthesized by Sol Gel Method

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Abstract: It has been proved that sol gel method is flexible, economical and less complex with respect to the other conventional methods for the synthesis of metal oxides or nano thin films. Due to less complexity, this process is extensively used in the field of fibres, microspheres, thin films, fine powders and monoliths. This review is a study and discussion of the influence of pH on ZnO and TiO2 thin film synthesized by sol gel. We are more interested in ZnO because it has a very wide band gap of 3.37 electron volts. The size and the entanglement of particles are strongly dependent of the acidity or basicity of the system (pH dependent). Due to the small particle size, the Van der Waals interaction is significant; this interaction increases exponentially as the particle size decreases. These facts favour the growth of clusters. In order to conserve the sample in a powder morphology with a high surface area, it is necessary to stabilize the gel. For low pH values a positive charged transition state is generated and groups –OR from the alkoxide are able to stabilize the solution better than the –OH groups. The nonhydrolyzed species will exhibit a high condensation velocity favouring the formation of long low branched chains and big size particles. Instead, if the catalyst is basic, the transition state charge is negative, the –OH group stabilizes the solution and the high-hydrolysed species will condense faster, favouring the formation of highly branched chains and small sized particles[26,27] We have seen that as the pH of solvent increases, the deposition time decreases and energy band gap decreases. Keyword: sol gel, nano materials, Semiconductor Metal Oxide,

I. INTRODUCTION

Sol-Gel is widely used for the fabrication of nano structured ceramic materials and thin films. In recent years, applications of semiconductor metal oxide nanoparticles are getting widespread covering different fields such as catalysis, optoelectronics, and sensor devices. Besides, increased surface to volume ratio, the parameters such as size, structure and elemental composition are considered to be key factor for promising applications of the nanomaterials. Among the metal oxide nanostructures, TiO2 has widely been explored for several technological applications such as catalysis, gas sensing and solar cells. Such applications of nonmaterial’ s have been found to depend strongly on the pH, crystalline structure, morphology, and particle size. It involves the conservation of precursor solution which is basically metal alkoxides or metal salts, into a nano structured in organic solid through in organic polymerization reactions catalysed by water. The basic reaction involved in the sol-gel process are:

A. Hydrolysis

$$\textbf{M-OR} + \textbf{H}_2\textbf{O} \longrightarrow \textbf{M-OH} + \textbf{ROH}$$

B. Condensation

$$\textbf{M-OR} + \textbf{H-O-M} \longrightarrow \textbf{M-O-M} + \textbf{R-OH}$$

Scientist defined the two words separately i.e. Sol and Gel, that is the liquid state of a colloidal solution is called the sol and Gel is the solid or semi-solid (Jelly like) stage of a colloidal solution is called the gel.

The process of sol-gel has been intensively investigated and used in recent years. The most important factors affecting its wide application are that the method is relatively easy rather than other coating processes and it provides a good enhancement for metallic biomaterial coating layers on the substrate [1-3]. Ethanol is mostly used liquid to dissolve phosphorous in the shape of phosphorous pentoxide while adding some amount of water in the solution to increase the hydrolysis, for production of sol [4]. One more point of attraction for the researchers is hydroxyapatite Ca5(PO4)3(OH)which is an inorganic biomaterial. HA (hydroxyapatite) has been studied for the medical purposes also. It is being observed that dense sintered HA has the application of bone replacement and also used for the defects in dental and immediate tooth replacement [5]. As above discussed, Sol-Gel process is very cheap and flexible either with the nano thin films or coatings and other wet chemical composition. It has been found that adhesive coating layer for strong bonding can provided with the help of this method [6].

Since Sol-gel is cheap and easy method, having a great coating property on the different substrates, the applications are increasing very rapidly. To get the more improvement in the process researchers are still working for the same. In addition of sol formation parameters like PH, solvents aging kinetics of molecules crack formation during drying and heat treatment are very important to be studied to understand the process and how to control the coating property [7,8,9,10]. One of the interesting fields that has been developed recently relates to hybrid materials that utilize sol–gel chemistry to achieve unusual composite properties.

II. APPLICATIONS OF SOL-GEL METHOD IN DIFFERENT METAL OXIDE FIELDS

Versatile, better homogeneity, low energy consumption and requirement of non-expensive equipment have boosted the use of Sol-gel in the area of nanotechnology. Metal oxide nanostructures like nanotubes, nanorods, nanoribbons, nanospheres, have been employed in the field of biomedical prepared by the sol gel. There are a huge number of fields in which this particular method has been employed. Since this method covers a very wide range of application so here, we are discussing only on two metal oxides first is Zinc oxide and second one is Titanium oxide.

A. *Metal oxide (MO) Structures.*

The synthesis of solid materials often involves wet chemistry reactions and sol-gel chemistry based on the transformation of molecular precursors into an oxide network by hydrolysis and condensation reaction [11,12]. Sol-gel prepared metal oxides have shown to exhibit excellent optical and electrical properties. The review of important MONSs derived from the sol-gel method helps us to understand the factors that could be taken into account for controlling the shape and size of the particles. In general, the solvents, additives, aging time and post heat treatment are few important factors that determine the shape and size of the building blocks of materials being synthesized [13,14]. Zinc oxide is a multifunctional material, which is used in the formation of thin films and being explored by many researchers. Sol gel is preferred for the preparation of ZnO structure. The ZnO thin film can be suitably applied in many fields, and it also has many functions such as UV light emitters, hydrophobic coating, transparent thin film in electronic devices, piezoelectric material, transducers, gas-sensing, and a transparent conductive oxide (TCO) layer in thin film solar cells. Some researchers used sol gel spin coating process (C.Jeffry Brinker and George W. Scherer, 1990) for the formation of ZnO thin film. Since sol gel process has advantage of controllability of composition and simplicity of process, different effects of annealing at the different temperature found by the optical properties [15].

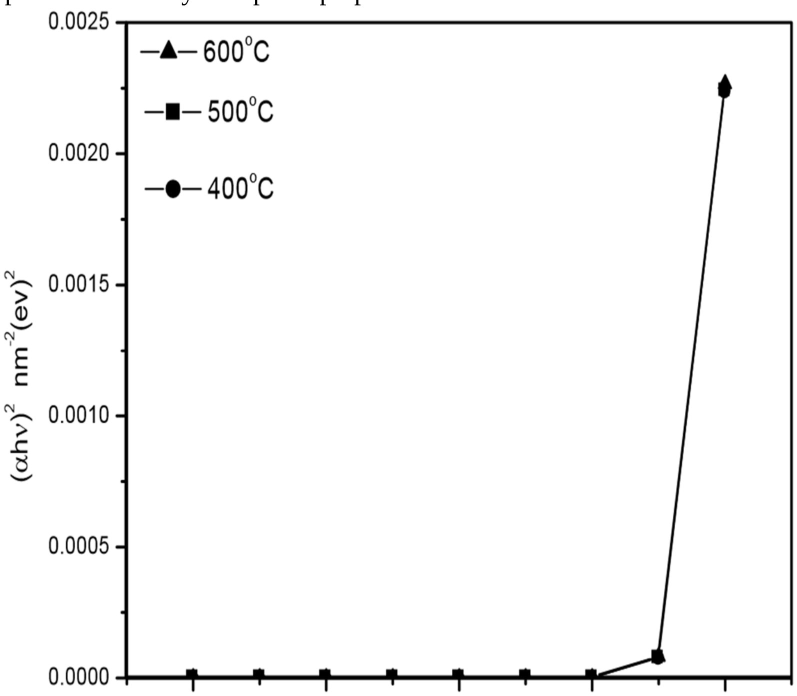

Figure 2.1.1. Plot of $(\alpha h\nu)^2$ vs. Photon energy hν for ZnO films at different annealing temperatures

The Figure 1 shows the energy of the ZnO at different annealing temperatures. The photoluminescence spectra of ZnO films showed prominent UV emission (~380 nm) and suppressed green emission (~500 nm). The temperature range will be increased in our future work for more generic applications [15].

Annealing temperature (ºC)	Band gap E_g (eV)
400	3.216
500	3.212
600	3.216

Table 2.1.2. Band gap Eg for ZnO films at different annealing temperature as estimated from Fig.1[15]

Somehow Scientists have been Developed a new sol gel route to synthesize some different transition and metal oxides aerogel. It can produce monolithic microporous, materials with high surface areas.

Materials that are commonly used in the sol-gel process is metal oxide. Furthermore, sonicator is used for mixing, and Zinc Oxide particles break. Zinc Oxide precipitates further heat in order to obtain a powder of nanoparticles of Zinc Oxide. The sol-gel method uses a lot of chemicals so it works on varying levels of acidity (pH) in the solution. The effect of pH contributes to the effects of hydrolysis and condensation during the process of forming a gel and the morphology of the resulting Zinc Oxide [17].

III. STUDY OF ZNO

Most common use of ZnO is in the sunscreen. This is because ZnO reflects the UV light. It is also being investigated to kill the harmful microorganisms in packaging. One of the many synthesized materials into nano-sized particles is Zinc Oxide. Zinc Oxide is a material that is currently widely studied. This is because ZnO exhibit optical, acoustic, and electrical properties allowing it a number of potential applications in the fields of electronics, optoelectronics, and sensors [16]. Due to excellent heat resistance anti-bacterial and anti-corrosion it plays an important role in current industry. So, it is desired to synthesize ZnO nanostructure with the most practical way i.e. sol gel. Because it has the ability to control the size of particle and control the reaction parameters.

ZnO nanoparticles were analysed by some researches by using XRD, EDX, FESEM. Result shows that ZnO has excellent purity. XRD shows the Zinc and oxygen peaks which indicates the crystallinity in nature. FESEM micrographs shows that synthesized ZnO have a rod-like structure. The obtained ZnO nanoparticles are homogenous and consistent in size.

The process parameters used are variations in pH. It has been seen that at higher value of pH has a fast to settle and very slow at low value of pH. The crystallite and particle sizes are inversely proportional to the pH values. Table shows the result:

pH	RPM (30 min)	Size of crystal	Deposition Time (minutes)	% ZnO	Energy Gap
7	3000	10.9±0.99nm	4320	42.9	-
8	3000	17.44±5.36 nm	1440	62.2	3.25
9	3000	-	600	-	3.24
10	3000	38.27±2.14 nm	480	64.7	3.23
11	3000	-	240	-	3.14
12	3000	74.04±41.77 nm	120	100	-

Table 3.1 The relationship between pH with deposition time [18]

etermining the composition of compounds is being done in some experiments using a search match with X-powder program. The search results matched the X-powder in a way fitting the data obtained by the percentage weight of the compound of synthesized ZnO at pH 12, 10, 8, and 7. So here we can conclude that pH is the one of the factors that effects the ZnO nanoparticles diameter using sol gel. In some papers it has been proven that greater the pH of sol gel greater the agglomeration so that size of particle gets bigger.

A. Structural Parameter of ZnO thin film by Sol gel at different Concentration

For the different concentration, for 500^0c the samples of different concentration from 0.25 ml to 0.75 ml shows that all thin films are polycrystalline wurtzite hexagonal structure and we can calculate the grain size of ZnO thin film by Scherrer's formula:

$$d = \frac{K\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the X-ray radiation

Zinc concentration (ml)	Particle Size (nm)	Thickness (m)	Energy band gap (ev)
0.25	23.92	0.26	3.3054
0.50	28.39	0.40	3.2695
0.75	25.24	0.44	3.2295
1.00	23.97	0.49	3.2757

Table 3.2 Zinc concentration, particle size and thickness [25,26]

The XRD results show that the films are polycrystalline wurtzite hexagonal structure and have no preferred orientation. The film with 0.5 m/l concentration has minimum value of strain and has larger particle size compared to other concentrations [25,26].

IV. STUDY OF TIO2

Titanium oxide is also known as flamenco, rutile, **titanium dioxide** and dioxo titanium. Titanium oxide **nanoparticles** are known for their ability to inhibit bacterial growth and prevent further formation of cell structures. TiO_2 nanoparticles are produced in the rutile and anatase forms. In sol gel processes, TiO_2 is usually prepared by the reactions of hydrolysis and polycondensation of titanium alkoxide, $(TiOR)_n$ to form oxo polymers, which are transformed into an oxide network. Crystalline titania has three modification phases which are rutile (tetragonal, $P4_2$ */mnm*), anatase (tetragonal, $I4_1$*/amd*) and brookite (orthorhombic, *Pcab*). Anatase-type TiO_2 has excellent photocatalytic activity and widely used as catalysts for decomposition of a wide variety of organic and inorganic pollutants. Many methods have been established for titania synthesis such as sol-gel technique [21-24]. Unlike larger particles, TiO_2 nanoparticles are transparent rather than white. Ultra Violet (UV) absorption characteristics are dependent from the crystal size of titanium dioxide and ultrafine particles has strong absorption against both UV-A (320-400 nm) and UV-B (280-320 nm) radiation [19]. Most manufactured nanoscale titanium dioxide is synthesized by the sulphate process, the chloride process or the sol-gel process [20] .

Synthesis of TiO2 using dip coating method or sol gel has been done by known researches and they found that the crystalline size of the nanoparticles is approximately 20nm and confirmed by XRD and FESEM. Optical absorbance of the prepared films was found between 360nm and 310nm which is corresponds to the band gap of TiO2 ~ 3.3ev and this band gap can only utilize light with wavelength below 400nm and thus only UV light is suitable since it has wave length range of 200nm-400nm. Typically, in sol gel method, the sol-gel derived precipitates are amorphous in nature. It is required for further heat treatment to induce crystallization. To induce transition from amorphous to anatase phase, generally an annealing temperature higher than 300 °C is required, and this will result in the dramatic growth of the particle sizes. However, titania for photocatalytic activity is dependent on both particle size and degree of crystallinity. Characterization of samples by x-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD results showed the existence of nanocrystalline anatase phases with crystallite size ranging from 7-14 nm. Results of photocatalytic studies exhibits that titania powder prepared at pH 9 has an excellent photocatalytic activity with degradation 74.7% within 60 minutes

V. CONCLUSION

It is observed that the energy band gap deceases slightly when we increase the concentration of the solution. It is obvious that concentration is directly proportional to the thickness of the thin film. In the case of ZnO energy band gap decreases when pH goes high. Increment in pH causes very short period of deposition time. we have seen that at pH value 12, the deposition time is less as compared to less value of pH and crystalline size is also big. Annealing temperature does not impact so much on the energy band gap. Studies exhibits that TiO2 powder thin film prepared at pH 9 has an excellent photocatalytic activity.

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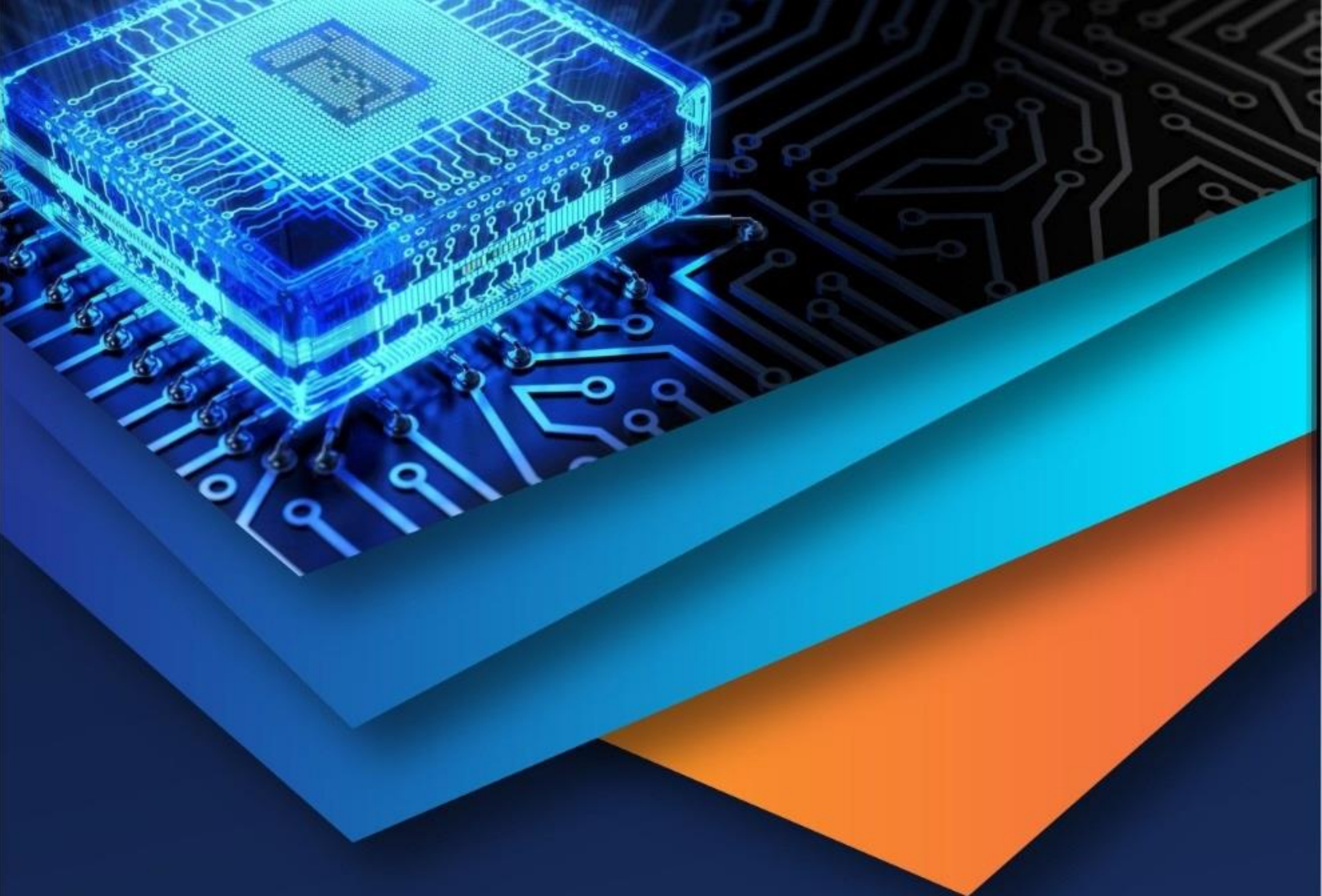

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