

Effect of pre-heating temperature on ZnO thin films prepared by ultrasonic atomization and pyrolysis technique

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Abstract: Highly textured ZnO thin films were prepared using ultrasonic nebulizer and pyrolysis technique in horizontal quartz reactor double zone furnace. The thin films were prepared by varying the first zone temperature from 25°C to 400°C while keeping second zone at 500°C while using 0.1M (300 ml) solution of Zn (NO₃)₂·6H₂O. The stock solution was converted into fine mist droplets using ultrasonic nebulizer (Gapusol 9001 RBI Meylan, France with frequency of operation 2.1-2.3MHz). The fine mist generated by nebulizer was allowed to pass and pyrolyzed onto previously kept inline glass substrates in horizontal quartz reactor heated using double zone furnace with first zone at room temperature (25°C) while second zone at 500°C. The thin film so prepared was termed as S1. Repeating above procedure and changing first zone temperature to 200°C, 300°C and 400°C respectively the films are called as S2, S3 and S4. The structural properties were analyzed by XRD patterns of the thin films. Microstructural properties of the films were studied using FESEM micrographs. The optical properties of the films were characterized using UV-Visible and Photoluminescence (PL) spectroscopy. The results are discussed and interpreted.

Index Terms: ZnO, Thin films, Ultrasonics cavitation and Pyrolysis, Nanorods.

I. INTRODUCTION

The ZnO is widely used materials in the medical, science and technology. The properties of the material mostly depend on the preparation condition of the materials. The world requires large quantity of nanocrystalline ZnO either in thin film or powder form at relatively low cost of synthesis. The ZnO has high mobility of conduction electrons and good chemical and thermal stability (Yamazoe, N., et al.,2003; Gaspar L., et al.,2017). It is a direct band gap wurtzite -type semiconductor. In nanocrystalline materials have large surface to volume ratio, due to this large surface area and interconnected particles give rise to a large

number of energy traps on the surface and grain boundaries (Fujishima, A., et al.,2008; Nelson J., et al.,2004; Thompson T., et al.,2006; Elser, M., et al.,2006).

In present investigation we report a simple technique to prepare porous and nanocrystalline ZnO thin films at relatively low temperature (500°C) with zinc nitrate used as precursor. The preparative conditions of the thin films were optimized so as to get highly textured ZnO thin films. The prepared thin films were studied for its structural, microstructural and optical properties. Ultrasonic nebulization and pyrolysis technique was used for thin film preparation. It is cheaper and easier technique to produce highly textured porous thin films, requiring no vacuum for processing. Additionally, this coating technique features the ability to control desired morphology characteristics. This technique prepares uniform, thin, well textured and crack free thin films with high transmittance and conductive properties.

II. EXPERIMENTAL

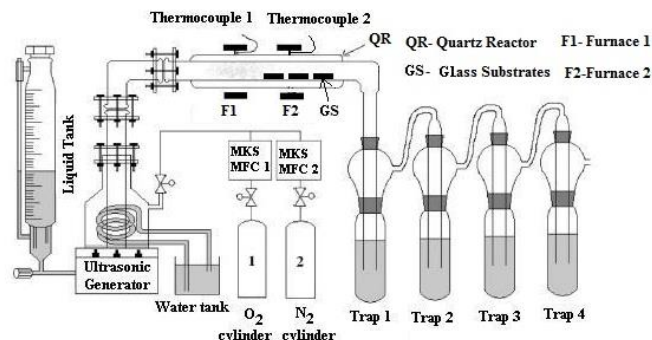


Fig. 1. Ultrasonic atomization and pyrolysis system to prepare thin films

The ultrasonic atomization and pyrolysis system used to prepare thin films is shown in Fig.1 (Patil L., et al.,2009). It consists of ultrasonic atomizer (Gapusol 9001 RBI Meylan,

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France with frequency of 2.1-2.3MHz), double zone quartz reactor, furnace, thermocouples with temperature indicator and trapping system. Ultrasonic generator produces high frequency waves having frequency in the range of 2.1-2.3MHz. The ultrasonic transducers convert a high frequency signal into mechanical vibrations. These vibrations are used to convert the precursor solution into the fine droplets (mist) or smoke.

A. Preparation of ZnO thin films

Ultrasonic atomization and pyrolysis technique (Fig.1) was used to prepare nanocrystalline ZnO thin films. In a typical synthesis, 0.1M zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] solution (300 ml) was prepared in double distilled water. This stock solution was stored into vertical cylindrical flask connected to ultrasonic atomizer. Ultrasonic atomizer was used to convert the solution into mist of fine droplets. The mist droplets were pushed using pressurized air from air compressor into horizontal quartz reactor placed into the double zone horizontal furnace. The glass substrates were placed into the quartz reactor (in IInd zone of the furnace) so that mist particles could pass from the top of the glass substrates and be pyrolyzed. The carrier airflow rate was optimized as 20kg/cm² to prevent segregation of mist droplets. The Ist zone temperature was kept at room temperature (25°C) and IInd zone temperature at 500°C. The mist droplets of solutions were passed for optimized time interval of 30 minute to get uniform thin films. Due to trapping system attached to rear end of reactor furnace, the rate of flow of mist was uniformly controlled which would help to get highly uniform thin films. After successful deposition, the films were removed and fired at 500°C for 1 hour in muffle furnace. The ZnO thin films so prepared were termed as S1. Repeating the same procedure to prepare ZnO thin films except first zone temperature was changed to 200°C, 300°C and 400°C respectively called as samples S2, S3 and S4.

Table 1: Dependence of size and shape of ZnO crystallites in the films on molarity

Sample name	Molarity $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution	Ist Zone II nd Zone temperature	Crystallite size (nm)
S1	0.1M	25°C_500°C	14.78
S2	0.1M	200°C_500°C	9.87
S3	0.1M	300°C_500°C	18.65
S4	0.1M	400°C_500°C	13.24

III. RESULTS AND DISCUSSION

A. Crystalline structure of ZnO thin films

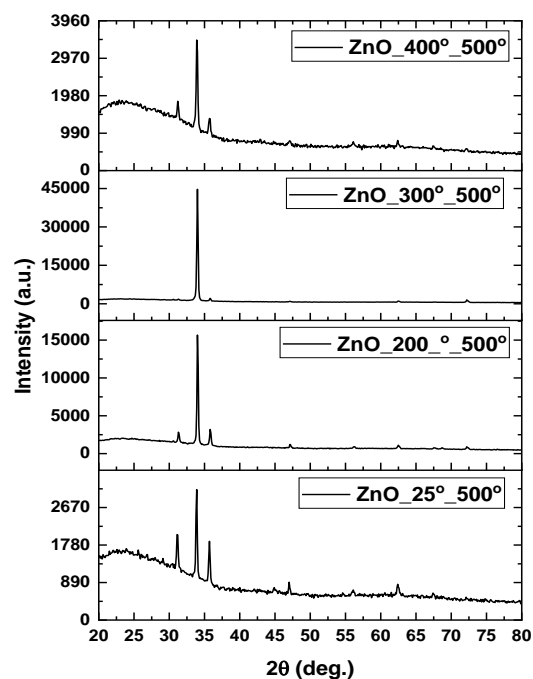


Fig. 2: XRD patterns of the ZnO thin films prepared using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution at different temperature gradient

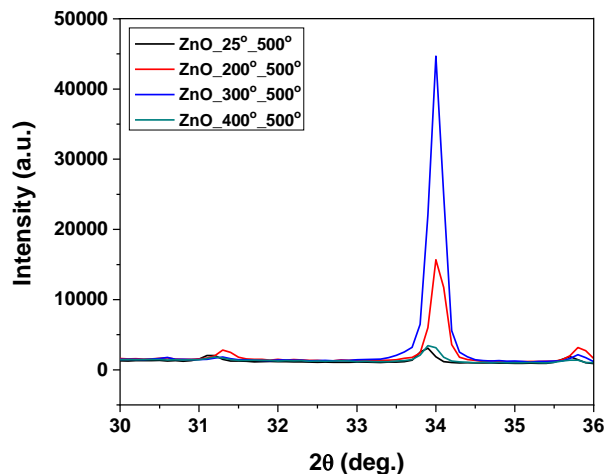


Fig.2 shows the XRD patterns

Fig.2 shows the XRD patterns of the films prepared using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution at different temperature gradient. The XRD patterns of the films are matching well with the standard data of ZnO with JCPDS file no.01-070-8072. Average size of crystallites associated with S1, S2, S3 and S4 ZnO thin film samples were determined using Debye-Scherrer equation. Average crystallite size and shapes were observed to be dependent on the temperature gradient of the preparation of thin films as presented in Table 1.

B. Microstructural studies of S1, S2 and S3 thin films using FESEM images

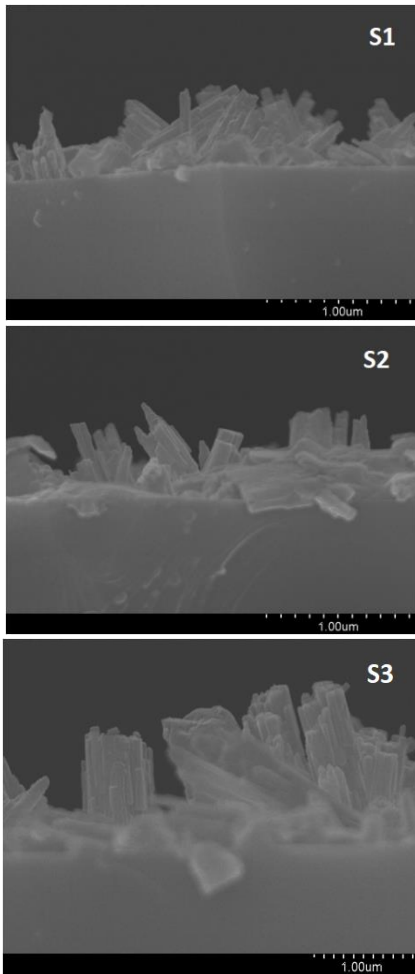


Fig. 3: FESEM images of S1, S2 and S3 thin films
Fig.3 shows FESEM images of ZnO thin films prepared at different conditions. FESEM images revealed that the thin films are consisting of bundles of nanorods. Most of the rods are vertically grown on the surface. The rods are being randomly distributed horizontally on the film surface. The average diameter of the rods is observed to be 200 nm. Due to presence of vertical nanorods the thin films have high surface area. The prepared highly porous thin films may be used in gas sensor fabrication.

C. UV-Visible spectroscopy of ZnO thin film samples

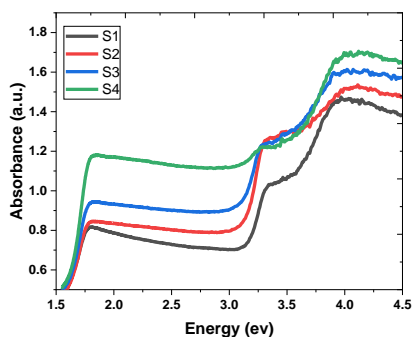


Fig. 4: UV-Visible absorption spectra of S1, S2, S3 and S4 samples

Optical properties of thin films were investigated by UV-Visible absorption. The absorption spectra of ZnO thin film S1, S2, S3 and S4 samples are shown in Fig. 4. The edge of absorbance is observed in the region of 3.0-4.0 eV for the films. The absorption edge is observed to be shifted towards smaller wavelength side with the increase in first zone temperature. This reveals that optical band gap increases with increase in temperature of first zone. This phenomenon is known as blue shift. The measured values of optical band gap energy of the ZnO thin films from the absorption spectra are tabulate in Table2.

Table2: Optical band gap

Sample name	Samples	Eg-Band gap energy (eV)
S1	S2	3.05
S2	S2	3.32
S3	S3	3.12
S4	S4	3.17

The band gap energy of ZnO thin film S2 was found to be largest as compared to band gap energies of samples S1, S3 and S4. It may be due to high crystallinity of the film as we can see from the XRD patterns of the films.

D. Photoluminescence spectroscopy

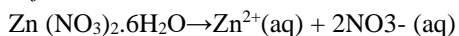
The room temperature photoluminescence (PL) properties of thin films were measured. Fig.5 shows PL emission spectrums of the thin films when excited at 420 nm. From PL spectrum it seen that there is large emission spectrum comes in visible range. The emission peaks in visible range may be caused due to surface defects (such as interstitial of metals and oxygen vacancies) in ZnO the thin films (Ilican S., et al.,2008; McCluskey M., et al.,2009). It is seen from the PL spectra that the intensity of the emission peaks increases with first zone temperature up to 200°C and further increase in first zone temperature decreases the emission intensity.

IV. DISCUSSION

In general, the wurtzite ZnO crystal has two polar planes: the low index planes that have high surface energy and in the metastable status. In addition, with the wurtzite hexagonal crystal structure, the six crystallographic equivalent nonpolar planes (parallel to the c-axis) are more stable due to relatively low surface energy (Vayssieres, L., et al.,2001). The formation of various shapes of ZnO nanocrystals is originated in the relative growth rates of different crystal facets. There is a large difference in growth rates of the wurtzite hexagonal ZnO crystals in different directions. According to the lowest energy principle, hexagonal ZnO crystals are inclined to grow along the [0001] facet to achieve the surface energy minimization, hence the growth velocity along the [0001] direction is faster than other growth facets, which lead to the formation of nanorods along the c-axis. The morphology of ZnO nanostructure can be tuned by changing

the growth parameters such as pre-heating temperature and the size and length of ZnO nanorods can be easily controlled during the chemical process. It can be seen from the SEM images in Fig. 3 that the effect of pre-heating temperature has a great influence on the morphology of the ZnO nanorods.

A. Formation of ZnO nuclei



B. Growth-Dissolution Recrystallization

The ZnO nanostructures undergo a reversible dissolution and recrystallization process via formation of zinc hydroxide, Zn(OH)₂. Each fine droplets of zinc nitrate precursor solution were passed through the quartz reactor leading to formation of one dimensional (1D) ZnO microrods. In the double zone horizontal quartz reactor furnace, the water is evaporated in the first zone and pyrolyzed in the second zone. The glass substrates are placed in the second zone, where the material is deposited.

The synthesis chemistry of the ZnO nanostructures is a complex process and mostly considered to include two main steps: the formation of growth units (the generation of a ZnO nuclei) and the incorporation of growth units into crystal lattice of the ZnO nanocrystals (subsequent ZnO crystal growth). Zn(OH)₄²⁻ complexes serve as basic growth units for the formation of ZnO nanostructures (Liang M., et al., 2014; Polsongkram, D., et al., 2008). When the concentration of Zn²⁺ and OH⁻ reaches to supersaturation, ZnO nuclei form. During the process, part of the Zn(OH)₂ colloids dissociates into Zn²⁺ and OH⁻. When the concentration of these growth units (Zn(OH)₄²⁻ complexes) exceeds the critical supersaturation level, the growth units become ZnO nuclei.

In an aqueous solution, the formed Zn(OH)₂ clusters dissolve in Zn²⁺ and OH⁻ ions due to plenty of OH⁻ ions. The growth units (Zn(OH)₄²⁻ complexes) being relatively more unstable as compared to ZnO nuclei, they would be transported to the surface of ZnO nuclei where it would be dehydrated. The rate of ZnO nucleation and transportation of growth units would be slow and systematic. ZnO is a polar material. Zinc and oxygen atoms are arranged alternatively along the c-axis. The growth rate along c-axis is faster than those along other directions. Thus, growth of ZnO nuclei occurs preferentially along the c axis of wurtzite structure ([0001] direction) to form rod-like structures.

SUMMARY AND CONCLUSIONS

- Nanostructured ZnO thin films were prepared successfully by ultrasonic atomization and pyrolysis technique. The thin films were prepared in double zone quartz reactor furnace with varied first zone temperature from 25°C, 200°C, 300°C and 400°C while kept second zone temperature at 500°C.
- The FESEM images of ZnO thin films showed that the topology changed due to change in preparative conditions (1st zone temperature: 25°C, 200°C, 300°C and 400°C).

- FESEM images of the thin films showed the ZnO thin films consist of rods. The bundles of nanorods were observed to be randomly distributed due to this the thin films are highly porous in nature.
- The rods deposited on surface of the film are seen to be mostly vertical to the surface of substrate; such films are reported to be technologically important and attractive.
- The size of crystallites associated with films was observed to be dependent on preparation condition. The films prepared at 1st zone at 200°C and 2nd zone at 500°C gives smallest crystallite size (9.87 nm) as compare to the other preparation condition.
- The band gap energy of the films was observed to be dependent on preparation temperature.
- The absorption edge was found to be shifted to lower wavelength side as we increase the first zone temperature from 25°C to 400°C.
- Photoluminescence emission spectrum of the thin films are found in visible range which may be due to the presence of defects on the ZnO rods. The prepared thin film material may be used in solar cells due to its high emissivity in visible range.

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