Influence of growth temperature on structure of Zinc oxide nanoparticles by solution evaporation method

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Zinc oxide (ZnO) has been famous for a wide range of application in Opto-electronic and Microelectronic devices. Until now, many different methods such as hydrothermal method, sol-gel method and co-precipitation method have been developed for the synthesis of ZnO nanostructure. In this research paper, ZnO nanoparticles were synthesized by simplest and cost effective technique of solution evaporation. The growth temperature varies from (100°C to 200°C) which plays vital role on nanostructure properties. The structural and surface morphology of ZnO nanopowder is characterized by the x-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that the synthesized ZnO nanoparticles have hexagonal wurtzite structure and average crystallite size increases with increasing temperature. SEM micrograph reveals that the particle sizes increase with increasing the growth temperature.

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1. Introduction

Semiconductor nanoparticles have created much interest among the researchers during the last few years because of their novel optical and transport properties which shows great potential for many optoelectronic applications [1]. The chemical, optical and electrical properties of a material can be tuned by varying the particle size. Zinc oxide (ZnO) has attained much attention within the scientific community as a 'future material'. It is an inorganic compound which usually appears as a white powder and insoluble in water. It is an important technological material. ZnO is a wide band gap (3.3 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications.

It has a large excitation binding energy of ~60meV and large direct-band gap energy of 3.37eV at room temperature [2,3], which is much larger Than the values for the other extensively used wide band gap Semiconductor materials, such as GaN(21−25meV) and ZnSe (20−22meV) [4].The large exciton binding energy of ZnO(~60meV) allows efficient excitonic emission even at room temperature, and thus gives promise for low-threshold and high-efficiency photonic devices [5]. The high exciton binding energy (60meV) in ZnO crystal can ensure efficient excitonic emission at room temperature. Zinc oxide (ZnO) is an n-type, direct band gap, II–VI semiconductor material [6]. Due to its high optoelectronic efficiencies relative to the indirect band gap group IV crystals, it is considered as a key material for variety of applications in the visible and near ultraviolet region[3]. ZnO has found numerous applications, such as gas sensors [7], biosensors [8], biological labels [9], solar cells [10], electrochemical cells, varistors, ultraviolet (UV) photodiodes, electrical and optical devices, and surface acoustic wave (SAW) devices.

The crystal structures shared by ZnO are wurtzite, zinc blende, and rocksalt. Zinc blende ZnO is stable only by growth on cubic structures; the rock salt structure is a high-pressure metastable phase forming at ~ 10 GPa. The wurtzite structure is most stable and thus most common at ambient conditions [6]. Numerous methods like physical vapor deposition (PVD) and chemical vapor deposition (CVD) have been developed to prepare ZnO nanoparticles into complex structures. However, these methods usually require high temperature, multiple steps and sophisticated equipments. On the contrary, wet chemical processes are attractive for some reason: they are low cost, less hazardous, and thus capable of easy scaling up; compatible with flexible organic substrates, growth occurs at a relatively low temperature; there is no need for the use of metal catalysts. Additionally, there are variety of parameters that can tune to effectively control the morphologies and properties of the final products .Wet chemical processes such as spray pyrolysis, hydrothermal process, sol−gel processing precipitation and co-precipitation are cost-effective and scalable and have been used in the synthesis of a wide variety of ZnO nanostructures. The precipitation method in particular has been successfully used to design different structures of ZnO.

Till now, many methods have been developed to synthesize zinc oxide nanocrystals including vapor phase growth, vapor- liquid- solid process, soft chemical method, electrophoretic deposition, sol-gel process, homogeneous precipitation, etc. The properties of the ZnO nanoparticles strongly depended on the microstructures of the materials, including crystal size, morphology (how the crystals are stacked) and orientation, aspect ratio and even crystalline

density. In this research, ZnO nanoparticles were synthesized by annealing the ZnO precursor at different temperatures. Over the past few years, various methods have been used to fabricate ZnO nanocrystals, vapor phase growth [2], vapor-liquid-solid process [3], soft chemical method [4], electrophoretic deposition [7], sol-gel process [8], homogeneous precipitation [9], etc. Among these methods, solution evaporation method (soft chemical method) [4] shows some advantages.(i) Nanometer- size nanoparticles at ambient temperature (ii)The reaction is carried out under moderate condition (iii) Nanoparticles obtained with different morphologies by adjusting the reaction condition (temperature) (iv) good controllability (v) Economical and cost effective method. The effect of reaction temperature, concentration of precursor and time of growth plays vital role on nanostructure properties.

2. Experimental procedure

2. 1 Synthesis method of ZnO nanoparticles

In order to synthesize the ZnO nanoparticles, the stock solutions of $Zn(CH_3COO)_2.2H_2O$ of (0.1 M) in 50ml methanol was prepared with the help of magnetic stirrer. To this stock solution 25ml of NaOH (0.2 M) solution prepared in methanol was added under continuous stirring. These solutions were transferred into oven and maintained at different temperatures from 100°C, 150°Cand 200°C for 6 hours. It was then allowed to cool naturally at room temperature. After the reaction was completed, the white product was obtained. Finally, in order to reveal the effect of temperature on ZnO nanostructure the structural and morphological characteristics have been done by XRD and SEM.

The following reaction occurred to synthesis ZnO nano-particles.

$$Zn(CH_3\,COO)_2.2H_2O + 2NaOH \rightarrow$$
$$Zn(OH)2+2CH_3COONa + 2H_2O$$

$$Zn(OH)_2 + 2H_2O \rightarrow Zn(OH)_4^{2-} + 2H^+$$
$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH$$

3. Results and discussion

3.1 X-ray diffraction (XRD) analysis

Fig. 1. shows the XRD pattern of ZnO nanoparticles synthesized at different temperatures 100°C, 150°C and 200°C. At 100°C the XRD pattern of ZnO nanoparticles illustrates the development of one diffraction peak. The diffraction peak of the zinc oxide (ZnO) appeared at the value of 34.435° is related to the ZnO (002) phase. Just one phase is tuned at 100 °C.

At 150 °C it is clear from the pattern of XRD that diffraction peaks appeared at 2θ values at 31.775°, 34.425°, 36.7524°, 47.552°, 56.6418°, 62.817°, 67.983° which are related to ZnO (100), ZnO (002), ZnO (101) ZnO (102), ZnO (110), ZnO (103) and ZnO (112) phases respectively. The XRD pattern of ZnO nanoparticles indicates that the peak intensity is different for every plane. Its mean that more phase are tuned at 150 °C.

At 200°C, the XRD patterns illustrate the development of diffraction lines appeared at 2θ vaues of 31.3966°, 34.4471°, 36.2427°, 47.4947°, 56.4495°, 62.5937°, 68.2187° and 89.7019° which are related to ZnO(100), ZnO (002), ZnO (101), ZnO (102), ZnO (110), ZnO (103), ZnO (112) and ZnO (203) phases respectively. When the sample was synthesized at 200°C and analyzed by XRD pattern, diffraction lines start to appear representing the development of the crystalline structure. All the diffraction peaks of the XRD patterns can be indexed to zinc oxide (ZnO) with the hexagonal wurtzite structure. By comparing with the standard card of bulk zinc oxide (ZnO) with hexagonal structure only few diffraction peaks of other impurities are present, which confirm that the substance synthesized belongs to zinc oxide (ZnO).

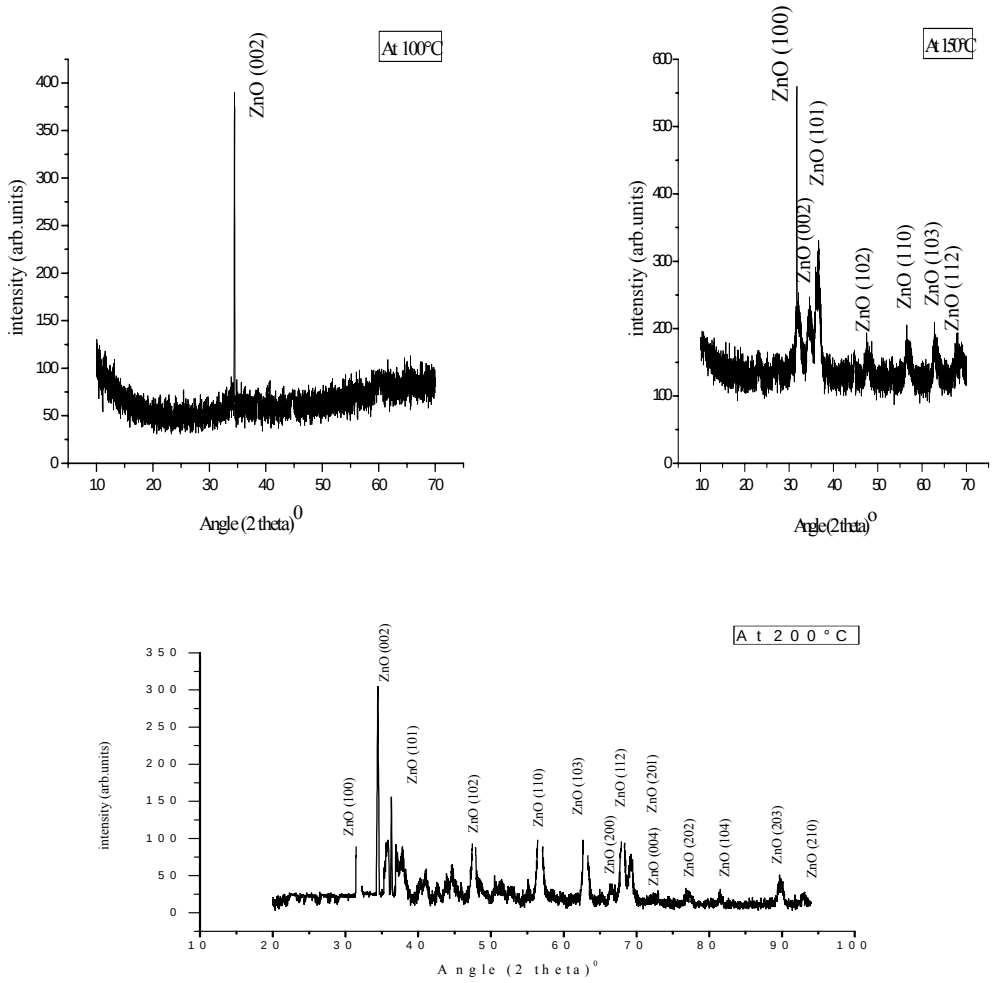

Fig. 1. Comparison between XRD patterns of ZnO nanoparticles synthesized at 100, 150 and 200 ^{0}C growth temperature.

3.2 Calculation of the average crystalline size by scherrer's formula

The crystallite size of the synthesized nanoparticles was determined from X-ray line broadening using the Scherrer's equation as follows:

$$t = k\,\lambda/B\cos\theta_B$$

Where,
t = crystallite size
λ= wavelength of the radiation (1.54 Å)
θ= Bragg's angle
B= full width at half maximum
K= constant (0.9)

We have determined the average crystallite size of ZnO (100), ZnO (002) and ZnO(101) diffraction peaks. Table 1 shows the average crystallite size of zinc oxide (ZnO) nanoparticles.

Table 1. Average crystallite size of zinc oxide (ZnO) nanoparticles synthesized at different temperatures.

Temperature (°C)	Size from (100) peaks	Size from (002) peaks	Size from (101) peaks	Average crystallite size (nm)
100	–	1.6	–	1.6
150	2.2	2.34	.23	4.8
200	2.6	.96	2.2	5.76

3.3 Effect of temperature on particles size

The size of zinc oxide (ZnO) nanoparticles was increased by increasing the temperature as shown in Table 2.

Table 2: Variation of crystallite size of zinc oxide (ZnO) nanoparticles with temperature

Sr.No.	Temperature (°C)	Average crystallite size (nm)
1	100	1.6
2	150	4.8
3	200	5.76

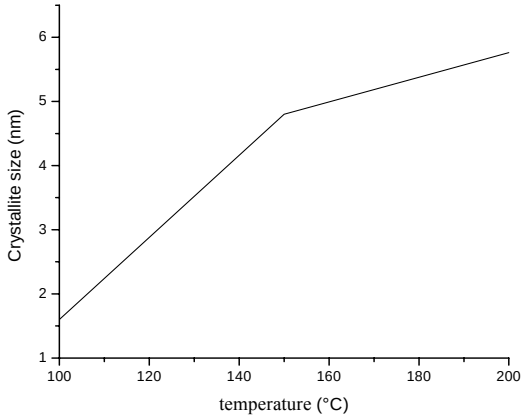

Fig. 2: Variation of particle size of ZnO nanoparticles synthesized at different temperatures

Reaction temperature is a significant parameter which influences the structural morphology of the particles as well as the size of particle. As the temperature of the reaction is increased there is increase in the size of the particle. In heating process when the particles are formed, they collide and either coalesce with one another to form a large particle. The process which occurs strongly depends upon the temperature of the reaction and available energy, due to this reason the size of the particle increases with increasing temperature.

3.4 Scanning electron microscope (SEM) analysis

In scanning electron microscope (SEM) high energy beam of electrons is used to scan the sample's surface in a raster pattern. When the electrons interact with the atoms of the sample's surface then it produce signals which give the information of that surface.

Fig. 3 illustrates the SEM images of zinc oxide (ZnO) nanoparticles synthesized at different temperatures 100°C, 150°C and 200°C. Actually SEM image contain the three kinds of particles namely:

(i) Cluster of the irregular particles
(ii) Bigger particles.
(iii) Rounded particles

Each cluster consists of several particles showing different shape and dimension. Some bigger and smaller particles are overlapped. It is also clear from the figure that the particles are distributed over the whole scanned area. Careful investigation reveals that at 100°C the average size of the particles is 346 nm.

At 150°C the SEM image demonstrates the formation of nanoparticles of different shape and size. These nanoparticles of different shape and size are linked to each other resulted in the formation of complex nanostructure. The average size of the nanoparticles is 445 nm. At 200°C the SEM image shows the formation of much bigger particles of different shape and size as compared to the previous SEM results. Careful investigation reveals that the average size of the particles is 912 nm. It is also concluded that the SEM microstructure of zinc oxide (ZnO) nanoparticles is changed with increasing temperature from 150°C to 200°C. The size of the particles increases from 346 nm to 912 nm as the temperature is increased from 100°C to 200°C. It means that the shape, size and distribution of the microstructure strongly depend on the temperature as well as on the other parameters like time and concentration.

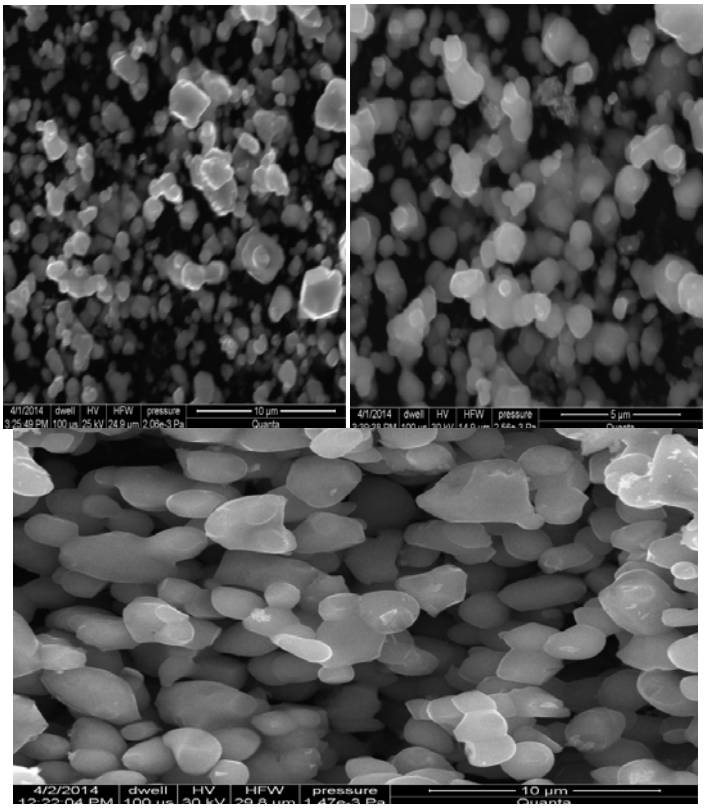

Fig. 3 Comparison between SEM images of ZnO nanoparticles synthesized at 100, 150 and 200 ^{0}C growth temperature

4. Conclusion

ZnO nanoparticles were synthesized using solution evaporation method. The effect of temperature on the structure, particle size, was investigated. The XRD analysis demonstrates that the nanoparticles have the hexagonal wurtzite structure and the particle size increases with growth temperature. The SEM analysis reveals the formation of nanoparticles of different shape and size at different temperatures. These nanoparticles of various shape and size are linked to one another resulting in the formation of complex nanostructure. The complex nanostructure image is spread over the whole scanned area. From the XRD and SEM analysis it is concluded that the particle size increases with the increase of temperature (100°C to 200°C).

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