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Role of annealing temperature and pH on structural and optical properties of ZnO nanocrystals by precipitation method

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Abstract : ZnO nanocrystals have been synthesized via simple precipitation method at different pH values. The synthesized nanocrystals are annealed at three different temperatures such as 400, 500 and 600°C respectively. The X-ray diffraction pattern shows that synthesized ZnO nanocrystals are of hexagonal structure and the grain size was found to be in the range of 30–60 nm. The results also indicated that the crystallinity of the nanocrystals improved with increase of pH values and annealing temperature. Scanning electron microscopic image shows that the surface morphology improves with increase of pH values. Optical absorption studies show that the bandgap has been found to lie in the range of 3.62–3.72 eV depending on pH suggesting the formation of ZnO nanocrystals.
Key words : pH values, ZnO nanocrystals, precipitation method.

1. Introduction

In recent years ZnO nanocrystals have attracted much interest because it has wide direct band gap and large exciton binding energy. Not only ZnO, all other semiconductor nanoparticles have attracted much attention in recent years due to novel optical, electrical and mechanical properties, which results from quantum confinement effects compared with their bulk counterparts. Compared with all other semiconductor nanoparticles, zinc oxide (ZnO) nanocrystals are the most frequently studied because of their interest in fundamental study and applied aspects in many areas, such as ultraviolet (UV) light emitting devices, sensors, laser diodes and other high speed electronic devices [1–4]. ZnO semiconductor has several favorable properties such as good transparency, high electron mobility, wide band gap and strong room temperature luminescence. It is also a material which is being used in non-electronic applications like optical brightener in wall colours, ingredient in sun cream and bone implants [5]. Several researchers have also investigated the different properties of ZnO nanocrystals including ultra violet and visible region emission. It is reported that structural imperfection and defects generally deteriorate exciton related recombination process and it is necessary to grow high quality crystals for all applications. ZnO nanocrystals have been synthesized by many research workers using different techniques like, molecular beam Epitaxy [6], chemical vapor deposition [7], aerosol pyrolysis [8],electrodeposition [9], sol–gel and precipitation method [10–14]. Out of these methods, the precipitation method is simple, inexpensive, non-vacuum and low temperature technique for synthesizing nanocrystals. This technique offers many advantages like, excellent control of the stoichiometry of precursor solutions, easy to modify the compositions, customizable microstructure, ease of introducing various functional groups, requires relatively low annealing temperatures and possibility of preparing over large volumes. In the present study, ZnO nanocrystals have been prepared using zinc acetate dehydrate and 2-methoxy ethanol by the simple precipitation method at room temperature. An attempt has been made to control the hydrolysis/condensation reaction in the precipitation of ZnO using mono ethanolamine. The effect of preparative parameter, pH, of the sol on the properties of the prepared ZnO nanocrystals has been studied.

2. Experiment

All chemicals used in this study were of high purity which was purchased from Sigma Aldrich. To synthesis ZnO nanocrystals zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) was used as zinc precursor. The required amount of zinc acetate dehydrate was mixed with 50ml double distilled water and a small amount of NaOH was dissolved in 50ml double distilled water and then this solution was added drop wise in the first solution; the slow addition yields a milk white solution. The obtained white solution was placed at room temperature for 24 hrs and then aged at an elevated hydrothermal temperature of 100°C for desired period of 48hrs for the nucleation and growth of ZnO nanoparticles. The resulting nanoparticles was washed with distilled water and the obtained solution was centrifuged at 5000 rpm for 10 min, the washing and centrifuging was repeated until solution had a pH of 5.0, and then the sample was dried at 100°C for 1hr. The ZnO nanocrystals have been prepared for another pH (=9) by using the same experimental procedure. The prepared nanocrystals are annealed at three different temperatures such as 400, 500 and 600°C respectively for 30 minute using a heating rate of 2°C/min. X-ray diffraction studies have been carried out using a PANalytical X-ray diffractometer with nickel-filtered CuKα (30 kV, 30 mA) and surface morphology of the film was studied using scanning electron microscopy (SEM; S-4100, Hitachi). Optical characterization of the films was carried out using UV–VIS–NIR spectrophotometer (Jasco V-570).

3. Results and discussion

X-ray diffraction pattern has been used to investigate the phase and particle size of the synthesized ZnO nanocrystals. Figure 1(a, b) shows the X-ray diffraction pattern of the ZnO nanocrystals prepared using pH=5 & pH=9 and annealed at different temperatures. All the diffraction peaks can be indexed to the wurtzite structure (hexagonal phase) of ZnO with fine crystallinity. The diffraction peaks present at 31.7°, 34.6°, 36.2°, 47.5°, 56.7°, 63.2°, 66.4, 68.0°, 69.1°, 72.3° and 76.9° are respectively indexed to (100),(002),(101),(102),(110), (103), (200), (112), (201), (004) and(202) planes of ZnO. The calculated lattice parameters are a=3.26Å and c=5.22Å and the values are in good agreement with the standard values (JCPDS No.36-1451). The results indicate that the products were consisted of pure phases. For all the annealing temperatures and pH values there is no additional peaks related to impurities. ZnO nanocrystals synthesized at both the pH values have the same hexagonal wurtzite structure. The growth rate of (002) peak has been found to increase with increase of pH, it is clearly shown in figure 1(b). The increase in intensity of (002) peak at higher pH values reveals high [001] growth orientation of the ZnO nanocrystals[15]. Furthermore, it could be seen that the diffraction peaks shown in both the figures are more intensive and narrower, implying a good crystalline nature of the as-synthesized ZnO nanocrystals.

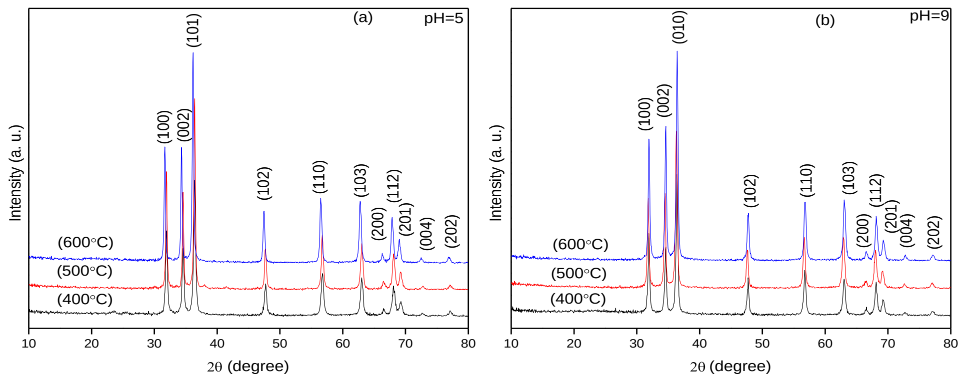

Figure 1.X-ray diffraction patterns of ZnO nanocrystals synthesized at (a) pH = 5 and (b) pH = 9

In addition, the broadening at the bottom of diffraction peaks shown in the figures also denotes that the crystalline sizes were small and in good agreement with the characteristic of nanosized particles reported in literature [10]. The average crystalline size (*D*) of the ZnO nanocrystals can be obtained from the Debye–Scherrer formula [16],

$$D = 0{\cdot}94\lambda/\beta\cos\theta$$

Where D is the mean crystallite size, β the full width at half maximum of the diffraction line, θ the angle of diffraction, and λ the wavelength of the X-ray radiation. The calculated crystallite sizes for different (hkl) planes are shown in table 1. From the table it is observed that both the pH values the particle size increases with increase of annealing temperature. For a particular pH value, the intensity of the diffraction peak increases with an increase of the heat treatment temperature, which is evident from increased intensity of (101) reflection and reduced full width at half maximum (FWHM). This is due to the transformation from amorphous to crystalline on heat treatment.

Table 1.Particle size of ZnO nanocrystals synthesized at different pH values

pH value	Annealing Temperature (°C)	Grain size (nm)					
		(100)	(002)	(101)	(102)	(110)	(103)
5	400	29.6	33.1	31.0	30.0	38.6	44.9
	500	42.0	47.5	41.0	44.8	47.3	50.6
	600	45.2	50.0	43.9	48.7	56.1	60.7
9	400	35.1	37.4	35.5	38.0	44.9	52.7
	500	36.7	39.6	36.5	40.2	47.8	53.1
	600	37.3	41.7	38.5	42.3	48.8	56.9

The scanning electron microscope images of the synthesized ZnO nanocrystals are shown in figure 2. The image clearly shows that the size and morphology of the synthesized nanocrystals were highly dependent on the pH value used.When the pH value is low, the nanocrystals smooth surface but at higher pH there is a small amount of nanorods agglomerated horizontally. This result shows that to synthesize nanorods higher pH value should prefer. At higher pH, the morphology of particles is to be found roughly spherical and homogenous; some of the particles have agglomerated.

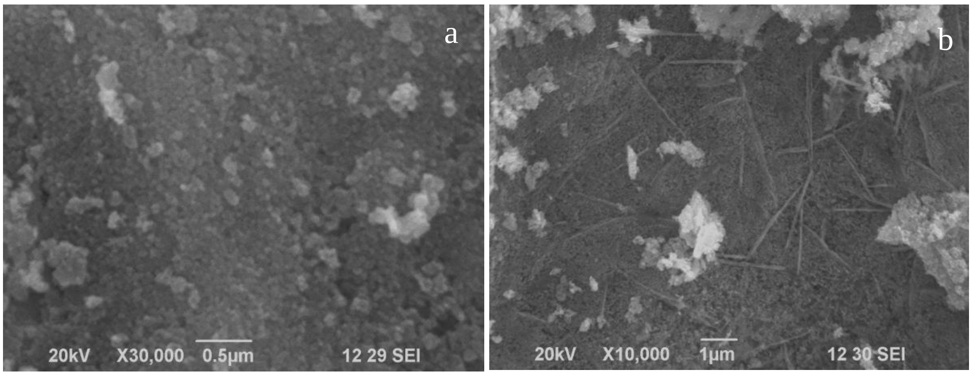

Figure2.SEM image of ZnO nanocrystals synthesized at (a) pH = 5 and (b) pH = 9

Figure 3 shows the UV-Vis absorption spectra of the ZnO nanocrystals prepared at different pH values and annealed at different temperatures. All the samples show sharp absorption in UV region and high transparency in the visible region. The absorbance of the ZnO nanocrystals is observed to decrease with increase in annealing temperature. This can be ascribed to the formation of larger particles with increase of annealing temperature which causes scattering of light.

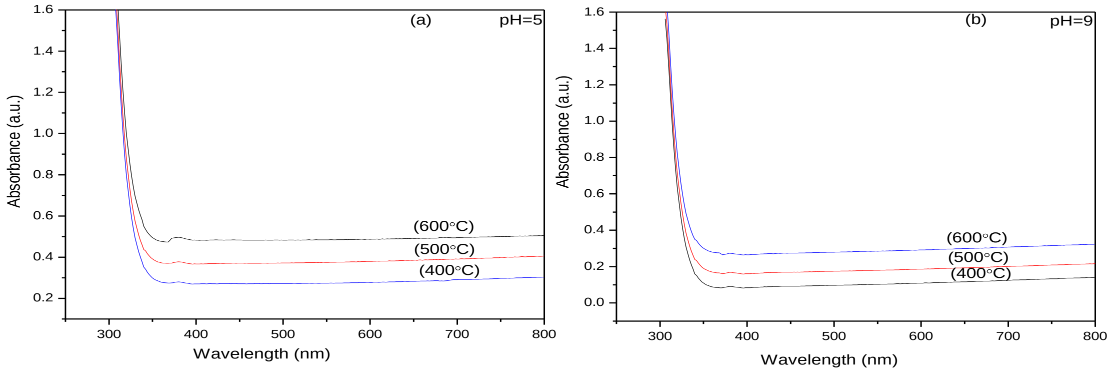

Figure 3. UV-visible spectra of the ZnO nanocrystals synthesized at (a) pH = 5 and (b) pH =9

By the extrapolation of the absorption edge onto the x-axis, band gap of the samples have been calculated and its values are tabulated in table 2. It should be noted that the band gap decreases with increase of annealing temperature. This may be due to the formation of larger nanocrystals at higher temperatures. The UV–Vis absorption spectra shows that absorption edge shifts to longer wavelength with increase of pH values and the red-shift of absorption edge can be attributed to the increase of ZnO nanoparticle sizes (formation of rod like structures) on increasing pH values. This absorption in the UV region was attributed to the transition from the ground state to a few defect related deep states. However absorption graph for both the pH values show excitations of unequal tail towards the higher wavelength regions it is due to scattering of light from the crystals.

Table 2.Band gap of ZnO nanocrystals synthesized at different pH values

pH value	Annealing Temperature (°C)		
	400	500	600
5	3.72 eV	3.68 eV	3.63 eV
9	3.66 eV	3.63 eV	3.62 eV

4. Conclusion

Using different pH values ZnO nanocrystals have been synthesized via simple precipitation method. The synthesized nanocrystals are annealed at different temperatures such as 400, 500 and 600°C respectively. The X-ray diffraction pattern shows that synthesized ZnO nanocrystals are of hexagonal structure and the grain size was found to be in the range of 30–60 nm. The results also indicated that the crystallinity of the nanocrystals improved with increase of pH values and annealing temperature. Scanning electron microscopic image shows that the surface morphology improves with increase of pH values. Optical absorption studies show that the band gap has been found to lie in the range of 3.62 – 3.72 eV depending on pH suggesting the formation of ZnO nanocrystals

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