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Growth of nanostructured ZnO by simple calcination method

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Abstract : Nanostructured ZnO were fabricated through a simple calcination method by heating a semisolid sol-gel of zinc acetate in a horizontal furnace at 900°C. The resultant powdered products were characterized by means of X-ray powder diffraction (XRD), transmission electron microscope (TEM) transmittance and photoluminescence measurements. XRD results showed a single phase hexagonal structure. TEM image showed that nanorod of average diameter 33 nm was formed when the sol-gel was calcined. The zinc accetate powder was also calcined directly which resulted in small hexagonal crystallites of size 46 nm. 95% transparency in the visible region was found in nano crystalline ZnO film on sapphire substrate. Photoluminescence measurements showed a blue shift in the band-edge emission due to the size effect.

Keywords ZnO, sol-gel, nanostructures, calcination, XRD, TEM, photoluminescence

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1 Introduction

Zinc oxide (ZnO) is a direct bandgap semiconductor having a energy gap of 3.37 eV and exciton binding energy of 60 meV at room temperature [1]. ZnO has many applications like chemical sensors [2,3], varistors [4] *etc*. Specially, now it is of great interest due to short wavelength optoelectronic devices [5,6]. Recently, much effort has been given in synthesizing low-dimensional ZnO such as nanorods [7,8], nanowires [9] and nanobelts [10] because of their important role in nanodevices. Single or polycrystalline ZnO nanomaterials were synthesized using different techniques like chemical or physical vapor deposition [7], thermal evaporation of oxide powder [11], two component chemical reaction or sputter deposition [12]. To obtain nano particles sol-gel is a option to start with. The product obtained by the sol-gel method generally consists of randomly arranged discrete nanoscopic sol particles. With this view in mind, we have attempted to fabricate nanostructured ZnO from sol-gel. Here, we report the growth of nanorods of ZnO by a single step calcination of a sol-gel of zinc salt. This would give us an easy way to obtain ZnO nanomaterials.

2. Experimental

A sol-gel of zinc accetate 2-hydrooxide ($Zn(CH_3COO)_2.2H_2O$) was prepared in dehydrated isopropanol by adding diethynolamine (DEA). The sol-gel was dried to a semisolid mass, which was kept in a quartz boat and calcined at 900°C in a horizontal tube furnace in air for 1 hour. The calcined product left in the boat was white and named as sample A. A thin film of ZnO was deposited on a well-cleaned sapphire substrate, which was kept above the boat, and this is called as sample B. We have also calcined direct zinc accetate powder at 900°C for 1 hour. In this case, the calcined product was yellowish white and named as sample C.

The structures of the samples were analyzed using Seifert X-ray diffractometer (model XDAL 3000) with CuK_α radiation. The microstructure analyses of the samples A and C were conducted using Hitachi H-600 transmission electron microscope (TEM). Optical characterization was done for sample B using Shimadzu UV/VIS spectrophotometer (model UV2401). Photoluminescence measurements of sample B was carried out in a fluorescence spectrophotometer (Hictachi F4500). The excitation wavelength used was 310 nm.

3. Results and discussions

Figure 1 shows the X-ray diffraction patterns of sample A, B and C. The peaks are assigned to (100), (002), (101), (102), (110), (103), (200), (112) and (201) diffraction lines respectively and can be indexed to crystalline ZnO phase indicating that the products consist of hexagonal ZnO phase. It important to mention here that the peak intensity of the (002) plane is

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comparable to that (101) but much higher than (100) plane for both samples A and B. However, for sample B this is unexpected since due to match in [0001] direction of sapphire substrate and a strong tendency of ZnO to grow along c orientation, the peak due to (002) plane should have dominated. Therefore although, the relative intensity of (110) plane in these patterns are much lower than that obtained from randomly distributed ZnO nanobelts reported earlier [10], the above results indicate that ZnO crystallites synthesized in case of sample A and B are randomly oriented. The XRD pattern of sample C again shows that peak intensity due to (101) plane is much higher than that of (100) and (002) planes similar to the report by Kong *et al* [13]. This indicates that crystallites obtained by direct calcination of zinc acetate powder are (101) oriented. The calculated lattice parameters a and c for all the samples are listed in the Table 1. The parameters are well consistent with the standard bulk values. Crystal size in each case was calculated using the Debye-Scherrer formula and also listed in Table 1.

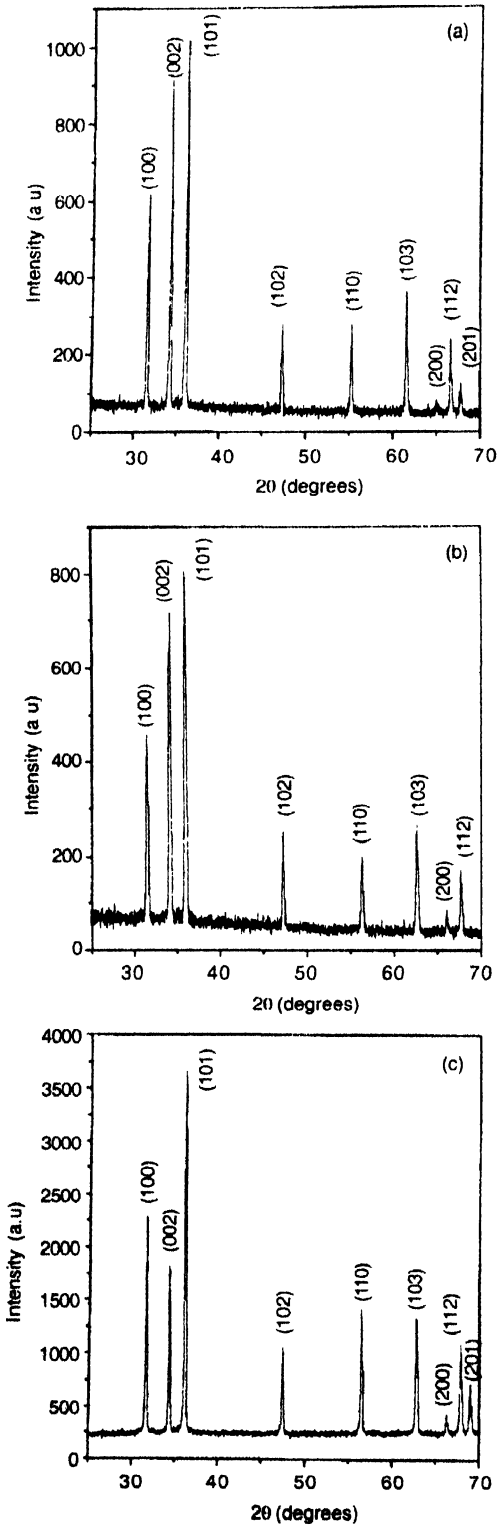

Figure 1. X-ray diffraction patterns of nanostructured ZnO : (a) sample A, (b) sample B, (c) sample C.

Table 1. Lattice parameters and crystal sizes of different samples calculated from the XRD data.

Sample type	Lattice parameters (nm)	Crystal size (nm)
Sample A	$a = 0.326$, $c = 0.523$	36
Sample B	$a = 0.327$, $c = 0.523$	25
Sample C	$a = 0.327$, $c = 0.521$	38

The morphology and microstructure of the samples A and C were further analyzed in TEM. Sample A was visualized under microscope mostly as an agglomerated product with occasional appearance of the nanorods. Figure 2(a) shows one of such nanorod, the average diameter of which is 33 nm. This value is close to the value listed in the Table 1 obtained from the XRD data. However, the diameter of the rod is not uniform throughout the length. It is known that resulting molecular structure configuration derived in this method is strongly dependent on

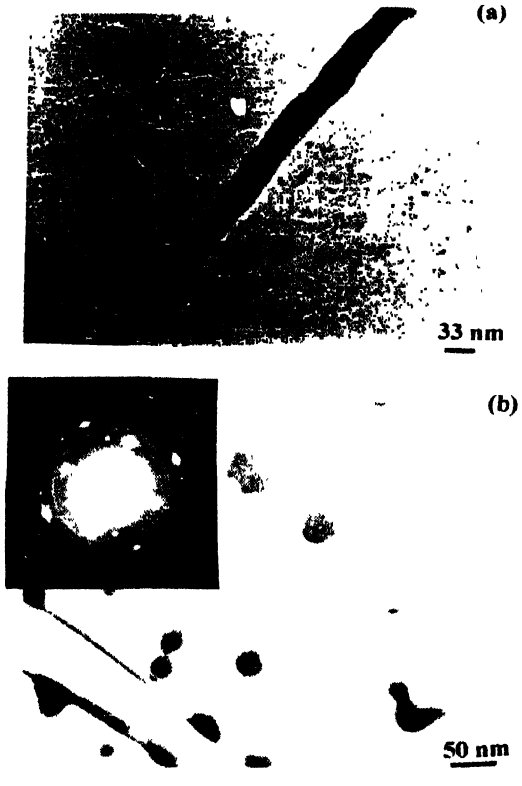

Figure 2. TEM images of nanostructured ZnO : (a) nanorod (b) nanocrystals. Selected area electron diffraction pattern corresponding to the nanocrystals is shown in the inset.

the processing parameter such as precursor, type of solvent and the pH. Therefore we expect to control the size and shape of the nanorod varying the process parameters. In this paper we report only the preliminary results of the synthesis of nanostructured ZnO. Figure 2(b) shows the TEM image of ZnO nanocrystals. Crystallites are having a average size of 46 nm. In this case also the crystal size calculated from the XRD data is close to the observed TEM size. Figure 2(c) shows the selected area electron diffraction pattern (SAED) taken from one single crystal of sample C. It shows that the crystal grows along [0001] direction.

Figure 3 shows the transmittance spectrum of the sample B. It shows that it is 95% transparent in the visible region and there is a sharp absorption band at around 359 nm indicating the formation of ZnO film on sapphire substrate.

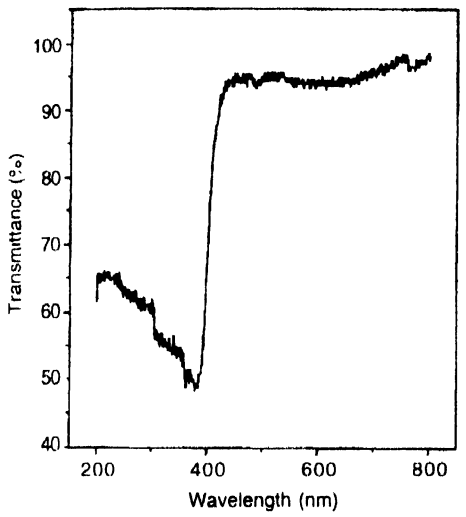

Figure 3. Optical transmittance spectrum of sample B

Figure 4 shows the PL spectrum of the sample B. The emission peak occurs at around 336 nm. It indicates that blue shift takes place when the value is compared to the bulk sample.

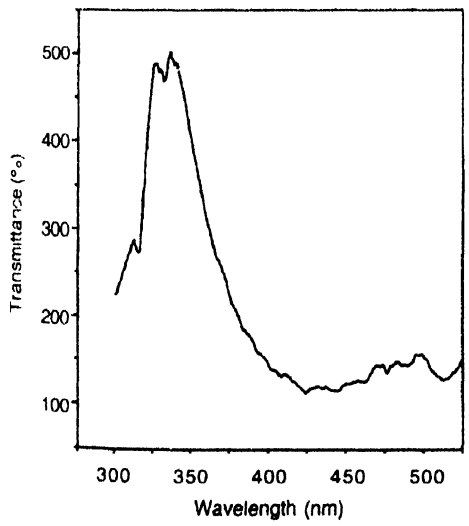

Figure 4. Photoluminescence spectrum of sample B

This is due to the decrease in the crystallite size. However, the reason for the shoulders in the emission peak might be due to the surface states since luminescence of ZnO is very sensitive to surface states which is dependent on the preparation methods [14,15].

3. Conclusion

In summary, nanostructured single phase hexagonal ZnO have been synthesized by a simple calcination method. Sol-gel calcination results in ZnO nanorods of average diameter 33 nm. Synthesis of well-defined nanorods might be possible if we can control the process parameters. The calcination of zinc accetate powder results in small hexagonal single crystals. Nanocrystalline ZnO film on sapphire substrate shows about 95% transparency in the visible region. Blue shift in the band-edge emission due to size effect has been observed in the photoluminescence measurements.

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