Preparation, optical properties of ZnO, ZnO:Al nanorods and Y(OH)$_3$:Eu nanotube

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ZnO, ZnO:Al nanorods and Y(OH)$_3$ nanotubes have been prepared by the chemical vapor deposition and liquid phase synthesis. ZnO nanorods with diameter of 50 – 100 nm and length of 5 $\mu$m have been obtained by the CVD method. ZnO:Al nanorods were synthesized by the hydrothermal method from ZnSO$_4$ and Al$_2$(SO$_4$)$_3$. Nanorods and nanotubes of Y(OH)$_3$ with diameter of 200 nm and length of several micrometers were prepared by the soft template method.

The crystal structure and morphology of rods and tubes were analyzed by the X-Ray diffraction and FE-SEM. The influence of fabrication conditions and Al, Eu concentration have been discussed.

1. Introduction

1-dimensional (1-D) nano-structural materials have gained much of interests in both research and development of functional materials for electronics, optoelectronics and electromechanics.

ZnO nanomaterials have many attractive properties such as a wide-band gap (3.37eV), large exciton binding energy (60 meV), high optical gain, and luminescent properties. These superior properties of ZnO make it suitable for short-wavelength optoelectronic applications such as the solar cell, piezoelectric devices, electroacoustic transducers, laser diodes and the semiconductor laser [1-3]. One-dimensional ZnO structures such as nanotubes, nanowires, nanorods, nanobelts have been synthesized by various methods including arc discharge, metal organic chemical vapor deposition, laser vaporization, pyrolysis, electrodeposition, sol-gel. Recently, several other new methods have been developed to fabricate 1-D nanostructures like template methods, the growth of 1-D nanostructures from different phases and/or solutions, self-assembling methods, etc. [4-5].

In the first part of this paper, we describe the preparation of ZnO and ZnO:Al nanorods by the chemical vapor deposition (CVD) and hydrothermal method. The effect of temperature on crystal structure, concentration of Al on the photoluminescent have been discussed. In the second part, we present the fabrication of Y(OH)$_3$ nanorods and nanotubes by using a polymer soft template. The formation mechanism nanostructures of Y(OH)$_3$ have been investigated in details.

2. Experimental

2.1. Preparation of ZnO, ZnO:Al nanorods

ZnO nanorods have been grown by the CVD method from Zn powders on the Si wafer (111) covered with Au or Pt. The carbotill e furnace system was used for the ZnO nanostructure. The CVD process was performed in the oven with an inner quartz tube under the argon flow of 0.5 to 1 l/min. Pure Zn nano powders (Aldrich) in alumina boat and Au-or-Pt-coated silicon wafer were set up in the quartz tube. Upon the argon flow the oven temperature was increased to 800°C in the time period of 10-60 minutes.

The Al doped ZnO nanorods were prepared by hydrothermal method from ZnSO$_4$·7H$_2$O and Al$_2$(SO$_4$)$_3$·18H$_2$O with the content of Al of 1, 3, 5, 7 and 10%. NaOH was added into the solution and stirred for 30 minutes at room temperature. Then the reaction solution was filled in Teflon container and
put in an autoclave. The reaction temperature was 180°C for 2h. After the reaction a clear solution was received. The Al doped ZnO product was precipitated in alcohol. Then the nanorods were separated by high speed centrifugation. The reaction product was washed with pure water and alcohol. The fine powder of ZnO:Al was obtained after drying at 105°C.

2.2. Preparation of Y(OH)3 :Eu nanotube

All the chemicals include NaOH, PEG with different molecular weight, Y(NO3)3, Eu(NO3)3 etc. were of analytical grade, with high purity (>99.9%). Deionized water was used throughout. Yttrium nitrate and PEG (Mw = 4000) were mixed up and added to? water at an expected volume. Then the reaction mixture was stirred continuously for 1h at room temperature. Alkali hydroxide of 10% was used for pH control in order to set an appropriate pH value range from 8 to 14. The stirring was carried out for half an hour or more. After that, the mixture was filled into Teflon container and put into an autoclave. The temperature of autoclave was maintained at different temperatures from 120°C to 200°C. The reaction time lasted from 16 hrs to 50 hrs. The purified procedure was performed by ultrasonic treatment, centrifugal separation and washing in de-ionized water. The obtained product was dried at 60°C in air.

2.3. Measurement

The morphology of the obtained product has been investigated by the FESEM (Hitachi) and TEM (JEM- 1010 instrument). The phase structures were revealed by X-ray diffraction measurements on XRD systems Siemens D5000, D5005.

Luminescent spectra were measured by the Spectrapro 2300i, CCD. The photoluminescence spectra were measured at room and low temperature in the spectral region of 350–600nm by using the excitation source of He–Cd laser of 325 nm or Ti sapphire Laser of 266 nm.

3. Results and Discussion

3.1 Structures of ZnO and ZnO:Al Nanorods

Fig.1 and Fig.2 are the X-ray diffraction pattern (XRD) of ZnO and ZnO:Al. In Fig.1 it can be seen that ZnO nanorod is a monophase crystal structure. The X-ray pattern of ZnO:Al in Fig.2 shows that ZnO:Al have several 2θ data of 31.8° ZnO(100), 34.39° ZnO (002), 47.5° ZnO(102), 57° ZnO(110), 63° ZnO(103).

Fig. 1: XRD of ZnO nanorods by CVD method 800°C, 60 min, Argon flow 1l/min.  
Fig.2 : XRD of ZnO:Al nanorods by hydrothermal method

FESEM images of ZnO nanorods can be seen in Fig. 3, 4, and 5. The ZnO nanorods were of 50-100 nm in diameter and 4-6 µm in length. Fig.5 shows the FESEM image of ZnO nanorods obtained by CVD 800°C for 30 minutes with argon flow of 0.5 l/m. Size and length of nanorods depends on temperature and time as well as the method (MOCVD, CVD or hydrothermal), the distance between Zn nanopowder source to the substrate, the speed of gas flux, Au or Pt deposition on Si wafer [6].
Fig. 3: FESEM ZnO Nanorods by CVD at 800°C, 30 min, Argon flow 0.8l/minute.

Fig. 4: FESEM ZnO nanorods by CVD at 800°C, 20 min, Argon flow 0.8l/min

Fig. 5: FESEM image of ZnO nanorods by CVD at 800°C, 30 min, Argon flow 0.5 l/min

Fig. 6 presents FESEM image of ZnO: Al nanorods synthesized by hydrothermal method. The ZnO:Al nanorods prepared by CVD are shown in Fig. 7.

3.2 Luminescence of ZnO, ZnO:Al nanorods

Luminescent spectra ZnO, ZnO:Al were measured at room temperature. Fig. 8 presents luminescence spectra of ZnO nanorods prepared by the CVD method. Luminescent spectra of ZnO nanorods grown on Silicon wafer covered by platinum show two bands. The band at 390 nm is attributed to the exciton recombination and the green emission at 507 nm seems to origin from defects. In the case of ZnO nanorods grown on Silicon wafer covered by gold, the green band of luminescent spectra is observed at 510 nm. The green emission is stronger for the sample covered with gold than the sample covered with platinum. However, the luminescent intensity at 390 nm is weaker for the former than the latter. Fig. 9 presents luminescent spectra of ZnO nanorods at 10K and 300K prepared by the hydrothermal synthesis upon the excitation of 325nm. At low temperature the luminescence spectra has structurally some sharp bands at 367, 375, 384 and 396nm. The broad band of emission is observed at temperature of 300K.
Fig. 10 presents the influence of concentration Al on luminescence. The luminescent intensity was the strongest for 7% of Al.

![Fig. 10: Luminescent spectra of Nanorod ZnO:Al with different concentration of Al 5,7,10% 325 nm excited](image)

3.3 Structures of Y(OH)$_3$ nanorods and nanotubes

XRD patterns of the obtained products are shown in Fig. 11 and Fig. 12. The obtained Y(OH)$_3$ nanorods and nanotubes are in hexagonal crystal phase [P63/m] with the lattice constants, $a=0.6248$ nm, $c=0.3525$ nm.

We found that Y(OH)$_3$ nanorods began to form at 170$^\circ$C in the PEG polymer with molecular weight of 4000. The forming process of Y(OH)$_3$ nanorods was completed at 190$^\circ$C (in Fig. 13). We also stated that Y(OH)$_3$ nanorods changed into nanotubes at 200$^\circ$C (in Fig. 14). This process not only formed cylindrical tubes but also hexagonal configuration. The cylindrical tubes have a dimension with outer diameters from 400-600nm and inner diameters from 150-300 nm. The hexagonal tubes have smaller diameters than the cylindrical ones. Both nanorods and nanotubes are yttrium hydroxides (Y(OH)$_3$). Moreover, yttrium oxides (Y$_2$O$_3$) nanorods and nanotubes can be created from yttrium hydroxides (Y(OH)$_3$) with a special annealing procedure.
3.4 Formation mechanism of the Y(OH)$_3$ nanorods and nanotubes:

The tubular shape of obtained products is clearly shown by HRTEM and TEM. Based on our research, we would like to explore further the forming mechanism of nanomaterial Y(OH)$_3$. It may be performed as follows: the first stage is formation of meta-stable complexes between Y$^{3+}$ cation and PEG, in which OH$^{-}$ group substitutes NO$_3^-$ to form Y(OH)$_3$. When the concentration of the OH$^{-}$ ions is high enough, they would aggregate to form small clusters or so called growing nuclei through a homogeneous nucleation. Because of their anisotropic crystal structure of Y(OH)$_3$, they tend to grow into nanorods. In order to form nanotubes Y(OH)$_3$, it is needed to have reversible exchange between the ions in the solution and the ones inside nanorods. To successfully form the hollow Y(OH)$_3$ structures, the out-diffusion of the Y(OH)$_3$ molecules inside the nanorods must dominate the agglomeration of the free Y(OH)$_3$ in the solution. The finished products of the process are cylindrical and hexagonal nanotubes.

4. Conclusions

ZnO, ZnO:Al nanorods were successfully prepared by CVD and by hydrothermal methods. The nanorods had the diameter of several ten nanometers, and the length of several hundred nanometer to micrometer.

Y(OH)$_3$ nanorods and nanotubes have been fabricated successfully by using the soft template synthesis in PEG polymer. The nanotubes growth process may be performed through three stages: complexing PEG polymer with Y(NO$_3$)$_3$, hydrolysis for formation of Y(OH)$_3$ nanorods and finally, the diffusion-controlled forming Y(OH)$_3$ nanotubes.

The luminescence of ZnO, ZnO:Al nanorods consisted of two bands originated from exciton recombination and from intrinsic defect. In the case of ZnO:Al nanorods, the emission is mainly in the orange spectral region.

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