Research Article

Study of Structural and Optical Properties of Zinc Oxide Rods Grown on Glasses by Chemical Spray Pyrolysis

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We have investigated morphological and optical properties of zinc oxide rods. Highly structured ZnO layers comprising with well-shaped hexagonal rods were prepared by spray pyrolysis deposition of zinc chloride aqueous solutions at $\sim 550^\circ\text{C}$. The rods were characterized by X-ray diffraction, scanning electron microscopy, atomic force microscopy, photoluminescence, and ultraviolet and visible absorption spectroscopy measurements. The deposition of the 0.1 mol/L solution at $\sim 550^\circ\text{C}$ resulted in crystals with a diameter of 400–1000 nm and length of 500–2000 nm. Sharp near-band edge emission peaks, centered at 3844 and 3680 Å, dominated the PL spectra of ZnO at 300 K and 6.2 K, respectively. In addition to this, absorption coefficient was determined by absorption measurement. X-ray diffraction, scanning electron microscopy and atomic force microscopy, results suggest that ZnO rods, prepared by spray pyrolysis, have high crystalline quality. This is desirable in nanotechnology applications.

1. Introduction

Zinc oxide (ZnO) is a commercially important material utilized in paints, rubber, catalysts, sensors, varistors, and so forth. ZnO exhibits semiconducting, piezoelectric, and pyroelectric properties [1, 2]. Nanostructured ZnO has a potential for application in nanotechnology [3, 4]. Structural, morphological, optical, and electrical properties of ZnO can be changed drastically by its doping with various metal cations [5]. Furthermore, ZnO thin films have recently been studied as an active channel material in thin film transistors [6, 7]. Chemically, ZnO is a simple compound; morphologically, however, this material is very rich in terms of the geometry of its particles. Many researchers focused on the investigation of the relationship between the synthesis route of ZnO on one side, due to their large exciton binding energy of ~ 60 meV at room temperature [8–13]. ZnO particles were largely prepared by using “wet” chemistry or pyrolysis, whereas the vacuum techniques prevailed in making thin ZnO films. The starting zinc compound, chemical composition of solvent, nature of the precipitating agent, pH, temperature, and time of aging influence the size and geometrical shape of ZnO particles [14].

In the past years, the ZnO micro/nanostructures with different shapes were synthesized by various approaches reported by many research groups. These methods include chemical vapor transport and condensation [15, 16], thermal evaporation [17], metal organic chemical vapor deposition [18], hydrothermal method [19], sol-gel method [20, 21], electrochemical deposition [22, 23], ion beam-assisted deposition [24], laser ablation [25], and sputter deposition [26].

In this study, ZnO rods were prepared by chemical spray pyrolysis technique. The spray pyrolysis is an attractive method to obtain thin films, since it has been proved to be a simple and inexpensive method and it is particularly useful for large area of nanotechnology applications. In addition, chemical spray pyrolysis has the advantage over the other methods in that it does not consume much time and is a cost-effective, catalyst, and template-free method to prepare ZnO nanostructures. Here, we report the direct growth of zinc oxide rods on glass substrate [27–30] by a chemical spray pyrolysis method. We have also studied the structural, morphological, and optical properties of the films with the aim of understanding physical properties of the obtained ZnO rods.

2. Experimental

ZnO rods were grown by a chemical spray pyrolysis technique. The spray solution was prepared dissolving ZnCl_2 (2.7256 g) in 200 mL distilled water. The initial pH value of solution was measured as 6. The starting solution was atomized at a frequency of 1.63 MHz by an ultrasonic nebulizer and by using dry air. The solution was mixed with magnetic mixer. Mixing process lasted for 30 min. The nozzle-substrate distance was maintained at 10 cm with 45 degree, and the substrate temperature was fixed at $\sim 550^\circ\text{C}$ by TET-612 temperature controller device on the metallic hot plate surface, because a flat ZnO film evolves into the the structured layer consisting of single-crystalline hexagonal elongated prisms at growth temperatures close to $\sim 500^\circ\text{C}$ and above [27]. The temperature of the metallic plate surface was totally stable. The substrates are normal microscope glasses which were cut with the dimensions of $10 \times 10 \times 1$ mm. Before loading into the system, the substrates were washed with detergent and then completely rinsed in methanol, acetone, and deionized water, respectively, and dried in air. Then, the substrates were progressively heated up to the required temperature, before being sprayed on. At this temperature, it was observed that the glass substrate became soft. The $5\text{--}6\text{ }\mu\text{m}$ diameter droplets were carried onto heated glass substrates. The flow rate of air used as a carrier gas was 2 mL/min. The duration of the film deposition was about 100 min. The colour of ZnO film was white, and it had very good adhesion to glass substrates. The structural characterization of the films was carried out by X-ray diffraction (XRD) measurements using a Rigaku D/Max-IIIC diffractometer with $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5418 \text{ \AA}$), at 30 kV, 10 mA. Surface morphology was examined by a JEOL JSM5610 model scanning electron microscope operating at 24 kV. The diameter and length of the rods were measured by a scanning electron microscope (SEM). In addition, morphology was also determined by atomic force microscopy (AFM). The optical characterization of the films was carried out by photoluminescence (PL) with an He-Cd ion laser as a light source using an excitation wavelength of 325 nm. So absorption coefficient was determined by UV-VIS absorption (UV) spectroscopy measurement.

3. Result and Discussion

3.1. Structural Properties. XRD patterns of the grown ZnO samples are shown in Figure 1. The diffraction pattern of grown sample shows a peak corresponding to (002) plane-reflection together with highly diminished peaks corresponding to other planes of wurtzite ZnO structure. The high intensity of (002) plane as compared with other planes clearly suggests the preferential growth of rods along the c -axis direction. The XRD pattern shows increase in the intensities of peaks due to reflections from all crystallographic planes of (100), (002), (101), (102), and (110) of wurtzite ZnO structure with predominant counts for (002) plane.

Taking SEM and AFM into consideration, we see that ZnO structures are spreading uniformly onto the sample surface, and vertically increasing from the axis c in Figures

FIGURE 1: XRD pattern of ZnO rods deposited on glass substrate.

2 and 3. The length of the ZnO rods is between 500 and 2000 nm, and the diameter changes between 400 and 1000 nm. The diameter and length of the ZnO rods acquired by SEM were confirmed by graphs acquired by means of AFM. These cross-section graphics are important that the same length or diameter is achieved on the plane sample. AFM results are in compliance with the SEM investigation. Additionally, the reason of the sunflower-like structures in the SEM pictures is unknown, but we thought that the reason of these structures may be related to the temperature gradient on the glass substrates (Figure 2(b)).

3.2. Optical Properties. Figure 4(a) was acquired from the room temperature PL spectra of the synthesized ZnO rods. Two peaks are observed in this figure: exciton peak in the left side and donor-acceptor peak in the right side. Figure 4(b) was acquired from the cryogenic PL spectra. Two peaks are observed in the spectrum at 6.2 K: one is a strong, dominated, and high-intensity peak at $3680 \text{ \AA}$ in the UV region; the other is a suppressed and weak band at $5500 \text{ \AA}$ in the visible region.

The UV emission is also called as near-band edge emission and originated by the recombination of the free excitons. The green band in the visible region, known as deep level emission, is generally explained by the radiative recombination of the photo-generated hole with the electrons which belong to ionized oxygen vacancies [31]. In our case, the UV emission is dominated over the green level emission. The weak peak is a result of donor acceptor pairs (DAPs) which can cause emission at room temperature. These DAPs are made up of dislocations or impurity in crystal. In general, the UV peak at room temperature is attributed to near band-edge (NBE) free exciton transition from the localized level below the conduction band to the valance band [32]. The emissions which are produced by DAP are decreasing by the temperature decrease because activity is decreasing by the temperature. The sharply peak is made up of exciton doublets which are not decomposed at the room temperature. According to PL data which is obtained in 6.2 K, the sharp peaks' duration increases at

(a)

(b)

FIGURE 2: SEM images of ZnO rods. (a) Hexagonal ZnO nanorods. (b) The result from temperature gradient-dependent structure deformation.

FIGURE 3: AFM image and cross-section graphic of the ZnO rods.

(a)

(b)

FIGURE 4: PL spectra of ZnO rods at (a) 300 K and (b) 6.2 K.

temperature decrease, so peak intensity increases and slides to the left side because decrement of temperature widens the band gap. The other peak seems like decreasing because of the increase of sharp peaks' intensity. It has been reported that the improvement in the crystal quality such as low structural defects, oxygen vacancies, zinc interstitials, and decrease in the impurities may cause the appearance of a sharp and strong UV emission and a suppressed and weak green emission [33]. So the presence of a strong UV emission and a weak green emission from the synthesized ZnO rods indicated that the grown structures have good crystal quality with less structural defects [34]. The absorption coefficient is one of the intrinsic parameters of the ZnO rods that was determined by fitting the absorption spectrum with an appropriate Beer-Lambert Law. The thickness of the ZnO rods was verified by the cross-section graphic of the AFM (Figure 3) and SEM images (Figure 2). The value of the energy and absorption coefficient calculation was carried out for the ZnO rods. It was found that the value of the energy is

3.35 eV and the absorption coefficient is 145125 cm^{-1} for the largest peak.

4. Conclusion

In this study, the ZnO rods on glass substrate were obtained by the ultrasonic spray pyrolysis method. The microstructures of ZnO rods were characterized by SEM, AFM images, and XRD patterns. Optical properties were obtained by PL spectrometer and UV-Vis measurements. Sharp near-band edge (NBE) emission peaks centered at 3844 and 3680 Å dominated the PL spectra of ZnO at 300 K and 6.2 K, respectively. In addition, structural analysis showed that the rods are *c*-axis-orientated ZnO wurzite crystals. The ZnO rods produced at optimum substrate temperature of $\sim 550^\circ\text{C}$ exhibited single phase of ZnO with preferred (002) orientation. Diameter and length of size ZnO rods were 500–2000 and 400–2000 nm, respectively. It was found that ZnO rods with good structural and morphological properties can be produced on glass. These results indicate that spray pyrolysis methods are a viable technique for producing high-quality ZnO rods for optical devices. At the same time, it is important to discuss the implementation of the presented results in this study for optoelectronic applications. The main issue in nanotechnology is to get devices in small size. The present work will contribute to the understanding of related photoluminescence, optical, structural, and morphological properties of ZnO nanomaterials.

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