Dynamics of the etching effects on the optoelectronic properties of ZnO nanorods

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Abstract. Zinc oxide (ZnO) is a very promising material for optoelectronic applications thanks to its wide direct band gap (3.4 eV), and a high exciton binding energy (60 meV). ZnO based nanostructures are presently being explored for a wide range of applications in nanolasers, nanogenerators, gas sensors, light emitting diodes and solar cells. In this study, we report the preparation of ZnO nanorods and the dynamics of their chemical etching under different concentrations. Characterization was carried out using X-ray diffraction, scanning electronic microscopy and photoluminescence. Thus, the study provides an investigation of the etching time and concentration effects on the optoelectronic properties. We found that all etching conditions are causing a remarkable proportional changes on the materials photonics as it is mainly changing the surface and creating defects. Hence, this study exhibits distinct advantages for optoelectronic devices.

1. Introduction

Zinc oxide (ZnO) is one of the most important semiconductors. Indeed, ZnO has a wide band gap (Eg=3.37eV), a direct band gap structure, a large exciton binding energy (60 meV), excellent chemical and thermal stability at room temperature [1]. In recent years, several publications considered one dimensional ZnO nanostructures such as nanorods [2], nanowires [3], nanobelts [4], nanotubes [5], and nanorings [6] etc. These materials have attracted great interest due to their promising applications in electronic, optoelectronic and sensing devices [7]. In particular, ZnO nanorods present excellent crystalline quality, high surface to volume ratio and high electron mobility [8]. Among these, ZnO nanorods have been extensively used in the recent past years due to their multifunctional device
applications in the areas of ultraviolet lasers [9], light emitting diodes (LEDs) [10], nanogenerators [11,12], field emission devices [13,14], gas sensor [15], and dye sensitized solar cell [16]. Presently, various methods have been developed to fabricate ZnO nanorods, such as physical vapor deposition (PVD) [17], chemical vapor deposition (CVD) [18], metal organic chemical vapor deposition (MOCVD) [19], molecular beam epitaxy (MBE) [20], pulsed laser deposition (PLD) [21], hydrothermal synthesis [22], chemical bath deposition [23], and chemical etching method [24]. Among all these techniques, chemical etching method is a low cost and environmentally friendly technique. This technique has been applied in industry over past decades. Wet chemical etching has great advantages due to its easy operation, time-saving, and capacity of anisotropic/isotropic etching [25]. Although the etching parameters consist of the etching time and the concentration of the etching solution, it is interesting to note that the etching rate also depends on the crystallographic orientation of the ZnO [26, 27]. Few studies discussed the effects of the etching parameters on the sizes and morphologies of ZnO nanorods. For example, Lei et al [28] demonstrated feasibility of the growth of ZnO nanorods by directly etching the substrate. Gan et al [7] electrodeposited well-aligned ZnO nanorods on ITO glass and analyzed the effects of both the etching periods and KOH concentration on the morphology of the ZnO nanotubes. Gruzintsev et al. [29] reported the effect of chemical etching on the luminescent properties of ZnOnanorods.

In this paper, ZnO nanorods were prepared by a chemical etching method under different concentrations. The concentration of the etching solution and the etching time were regulated respectively and their effects on the morphology of the ZnO nanorods were also discussed in details. The samples were then characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and photoluminescence (PL) to investigate their structural and optical properties.

2. Experimental method
ZnO precursors used in this work were purchased from Sigma-Aldrich. To synthesize ZnO nanorods, an equi-molar aqueous solution of 0.1 M zinc nitrate (Zn(NO3)2) and hexamethylenetetramine (C6H12N4, HMT) was prepared using deionized water. This mixture was heated at a constant temperature of 90°C in an oven for 24 h. The obtained materials were deposited on Si (100) substrates and dried at 50°C for 2 hours. Then, the formed films were etched with solutions of NaOH of different concentrations.

3. Results and discussion
3.1. Structural properties
Figure 1 shows the XRD pattern of pure ZnO and ZnO nanorods prepared at different concentrations by the chemical etching method. All the diffraction peaks matched greatly well with hexagonal phase without getting any additional peaks except the peaks which are characteristic of ZnO. The intense peaks in the XRD pattern of the samples clearly showed the formation of hexagonal wurzite phase of ZnO corresponding to (101) reflection plane in all samples, which is the preferred orientation. In addition, the intensity of the peaks (100) and (002) decreased with increasing etching concentration, which can be due to the incorporating of impurities in the lattice of ZnO. Also, the reduction in the intensity of XRD spectra is observed with the increasing concentration, this can be attributed to the dissolution of (100), (002) and (101) during the etching process.
Figure 1. XRD patterns of the pure ZnO and ZnO nanorods etched at different concentrations.

Figure 2 shows the XRD pattern of pure ZnO and ZnO nanorods prepared with different etching times 30 min, 60 min, and 120 min, respectively. All the diffraction peaks matched very well with the hexagonal wurtzite phase of ZnO and no other crystalline phases are detected. Also, the high intensity (101) peak in the XRD pattern compared to (100) and (002) peaks, corresponding to the reflection plane in all samples, which is the preferred orientation. The intensity of the (101) peak of the ZnO nanorods decreased with increasing etching time from 30 min to 60 min, and then increased with further increasing etching time to 120 min. This can be explained by the reduction of crystallinity following directions (100) and (002).

Figure 2. XRD patterns of the pure ZnO and ZnO nanorods etched with different etching times.

Figure 3 shows SEM images of pure ZnO nanorods and etched by the NaOH solution for 60 min. From the image (a), it can be observed that the ZnO nanorods with high density and well-defined hexagonal cross sections were grown vertically. The average diameter of the nanorods was about 400 nm and the surface of ZnO nanorods was very smooth. After etching, these nanorods for 60 min, large scale hexagonal ZnO nanorods preserve the same shape and diameter as before. However, image (b) shows clearly several defects on the surface of ZnO nanorods after etching treatment.
Figure 3. SEM images of zinc oxide nanorods: (a) as-grown, (b) after etching.

3.2. Optical properties

The PL spectrum was measured to analyze the optical properties of ZnO nanorods and defect types of the products which are important for optoelectronic applications. Figure 4 below presents PL spectra of the as-grown ZnO and ZnO nanorods prepared by the hydrothermal method. All the PL spectra show a distinct emission located around 560 nm. As can be seen in this figure, the intensity of the PL spectra is initially increasing as a function of the etching concentration. The differences in the PL band-edge emission peaks could be attributed to the increasing concentration of defects in the ZnO nanorods. A higher broad green-band emission peak is owing to the attendance of a number of ionized oxygen vacancy (V0+) defects. Guo et al. have found that the oxygen vacancy results from the concurrence among O atoms entering the ZnO lattice and those exciting this lattice by evaporation [30].

Figure 4. PL spectra of the as-grown ZnO and ZnO samples etched at various concentrations of NaOH solution.

Figure 5 shows PL spectra of the as-grown ZnO and ZnO nanorods etched for different times. The peaks shown in this figure are the PL band-edge emission peaks of ZnO located at approximately 560 nm and are commonly attributed to oxygen vacancies [31]. Up to 60 min, the intensity of the emission
peaks increases with increasing the etching time. However, as the samples were etched over longer periods of time, the intensity of the PL spectra starts to decrease. As viewed in this figure, the intensity of the green band emission peak decreases (to 120 min). This can be explained by the fact that the effect of etching has a saturation on the emission. In other words, to increase the intensity of the peaks, the etching should not exceed a given time. Another explanation could be that the intensity of the PL band emission peak, which decreases after 120 min, is awarded to the decrease in the surface to volume ratio of the ZnO nanorods that conducted the decrease of the PL band edge intensity which is in good agreement with previous work [32].

Figure 5. PL spectra of as-grown ZnO and ZnO nanorods etched by NaOH solution for different times.

4. Conclusion
In summary, we have synthesized ZnO nanorods by the hydrothermal method and etched them chemically. The analysis of X-ray diffraction showed that the samples had hexagonal wurtzite structure with (101) as a preferred orientation for the growth of the ZnO nanorods. After etching, SEM images also showed some defects in the samples which lead to a change in the surface morphology of the ZnO nanorods. Furthermore, PL spectra showed that the peaks intensity increases with increasing etching time. These results may be explained by the decrease in the surface to volume ratio attributed to the longer etching time. Therefore, this process can be used to enhance the efficiency of some optoelectronic devices.

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