Research Article

Influence of pH, Precursor Concentration, Growth Time, and Temperature on the Morphology of ZnO Nanostructures Grown by the Hydrothermal Method

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We investigated the influence of the pH value, precursor concentration (C), growth time and temperature on the morphology of zinc oxide (ZnO) nanostructures. The pH of the starting solution was varied from 1.8 to 12.5. It was found that the final pH reaches an inherent value of 6.6 independently of the initial pH solution. Various ZnO structures of nanotetrapod-like, flower-like, and urchin-like morphology were obtained at alkaline pH (8 to 12.5) whereas for pH solution lower than 8 rod-like nanostructures occurred. Moreover, we observed the erosion of the nanorods for a pH value less than 4.6. By changing the concentrations the density and size were also varied. On going from a high ($C > 400$ mM) to lower ($C < 25$ mM) C , the resulted ZnO nanostructures change from a film to nanorods (NRs) and finally nanowires (NWs). It was also found that the length and diameter of ZnO NRs follow a linear relation with time up to 10 hours, above which no further increase was observed. Finally the effect of growth temperature was seen as an influence on the aspect ratio.

1. Introduction

Zinc oxide (ZnO) is a promising material with wide bandgap of 3.4 eV and relatively large exciton binding energy of 60 meV [1]. Zinc oxide is also characterized by having excellent chemical stability, nontoxicity, and good electrical, optical, and piezoelectric properties [1, 2]. This material also possesses a rich family of nanostructures (NSs). It has been predicted that in general NSs will play an important role in the future in a variety of practical applications, including optoelectronic devices, for example, solar cells [3], UV sensors [4], biosensors [5], and light emitting diodes [6–8]. For these applications, it is essential to have a thorough understanding of the growth mechanism to achieve the desired morphology of the ZnO NSs needed. Since the properties of ZnO NSs strongly depend on its morphology and shape, it is also essential to precisely control their size, shape, and surface architecture to utilize its properties in different practical fields. However, many methods have been applied to the synthesis of ZnO NSs, such as metal organic chemical vapor deposition (MOCVD) [9], electrochemical

deposition techniques [10], sputter deposition techniques [11], and pulse laser deposition method [12]. But those methods require severe reaction conditions, such as high temperature, accurate gas concentration, and flow rate or complex processes. So it is important to find a simple, low-temperature method for the synthesis of ZnO NSs and find a way to control the growth parameters. Compared with the above synthesis processes, the ZnO NSs were grown by using the hydrothermal method. This growth method showed some advantages compared with others such as the use of simple setup, relatively low temperature, large area deposition, and low cost and is environment friendly. There are several parameters in the hydrothermal method that can affect the growth of the ZnO NSs such as seeding of the substrate which increases the density and alignment of the NSs [13], thickness of the seed layer which can be controlled simply by the speed of spin coating, and also presence of impurities in the seed layer which can strongly influence the growth and crystallinity of the ZnO NSs [14]. Other parameters like angle of the inclination, for example, whether the substrate is placed vertically or inclined with the walls of

heating bath, temperature, time, concentration, and pH have also an influence. Using different precursors from the one used here, the temperature was found to affect the synthesis of ZnO nanorods, for example, the length and diameter of the NRs increased with increasing the temperature [15]. It has been reported that the time is largely influencing the ZnO NRs diameter; longer synthesis time leads to larger diameter NRs [16]. The dimension of ZnO NRs was also found to be affected by the zinc ions concentration [16]. The role of the pH on the hydrothermal growth of the ZnO NRs was examined, and it was shown that the effect of the pH is crucial because hydroxide ions (OH^-) are strongly related to the reactions that produce the ZnO NSs [17–19]. Nevertheless, in the above-mentioned published results either only one parameter was considered or it was for a different precursor than the one used here. Furthermore, none of the published reports have been used to examine the growth of the ZnO NSs under a pH value $\ll 7$. Therefore, several fundamental reaction parameters need to be addressed to understand its influence on the growth.

In this paper, we present a study of the effect of different parameters on the morphology of ZnO NSs. These parameters are the solution pH (within a range of 1.8–12.5), temperature, time, and precursor concentration. We have conducted a systematic morphological and structural study of the grown samples. The results demonstrate that ZnO NSs morphological and structural characteristics can be controlled by adjusting the above-mentioned parameters.

2. Experimental Procedure

All the chemicals used in this study were of analytical reagent grade purchased from Sigma-Aldrich and used without further purification. The aqueous solutions containing the growth precursors were prepared using deionized water (DI) as a solvent. Silicon (100) substrates were chosen for the growth and were cleaned in ultrasonic bath using acetone, IPA (isopropyl alcohol), and DI water to remove dust and surface contamination. Then, they were etched by diluted hydrofluoric acid (HF) solution to get rid of the native oxide layer. For the ZnO NSs growth, a seed layer has been prepared using zinc acetate solution in ethanol as described in [20], and it was spin-coated on the substrates two times at a spin speed of 1000 rpm for 30 seconds, followed by soft baking at 120°C for 5 min. Figure 2(a) shows the atomic force microscope (AFM) image of seed layer coated substrate and its height profile which shows an average height of the particle 10–15 nm. Seeding of the substrate with ZnO nanoparticles was found to lower the thermodynamic barrier by providing nucleation sites and thus it is an important parameter to achieve uniform growth of ZnO NSs through hydrothermal process [20]. The same procedure and conditions of depositing the seed layer are applied to all samples used in the experiments. The aqueous solution for the growth of ZnO NSs was prepared using equimolar zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%) and hexamethylenetetramine (HMT) ($\text{C}_6\text{H}_{12}\text{N}_4$, 99.5%). The solution was then transferred into different sealable glass beakers.

FIGURE 1: Plot of initial versus final pH of the precursor aqueous solution for the ZnO NSs in 5 hrs of growth time.

To investigate the role of the pH on the growth of the ZnO NSs, the solution was adjusted to different pH ranging from 1.8 to 12.5, and in each beaker a preseeded substrate was suspended vertically for 5 hours (hrs) at 90°C in an ordinary oven. The pH values were varied by adding precise amounts of nitric acid (HNO_3) or ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) (procedure A) and hydrochloric acid (HCl) or sodium hydroxide (NaOH) (procedure B) to the aqueous solutions as pH controlling agents. The inherent pH of the solution was 6.6. At the end of the growth, the substrates were taken out of the solution and rinsed several times with deionized water then they were dried using high purity N_2 gas at room temperature, and the pH of each solution was monitored after the growth ended. All the pH measurements were carried out with a pH meter from Metrohm Instruments.

To observe the effect of time and temperature, we used the same aqueous solution (100 mM concentration) for the growth of ZnO NRs at different reaction times (1 to 20 hrs) at 90°C and different temperatures (50°C to 110°C) for 5 hrs, respectively. To examine the influence of the concentration, an equimolar different precursor concentration solution (5 mM to 400 mM) was prepared for a growth time of 5 hrs at a temperature 90°C . The characterization of the NSs was performed using field emission scanning electron microscopy (SEM) and X-ray diffraction (XRD).

3. Results and Discussion

3.1. Influence of pH on the Growth of ZnO NSs. For the growth of materials with chemical route, the pH value has always an important influence on the final products. In order to better understand the effect of the pH on the growth of ZnO NSs, the initial and the final pH values were carefully measured before and after the growth. Two sets of chemicals were used to vary the pH of the reactants, that is, procedures A and B. The different initial pH ($\text{pH}_{\text{initial}}$) values of the

FIGURE 2: (a) shows the AFM image of the seed layer and the corresponding height profile. (b) SEM image of ZnO NSs on Si substrate grown with different aqueous solutions of pH value 1.8; (c) at pH value of 4.6; (d) at pH value of 6.6; (e) at pH value of 9.1; (f) at pH value of 10.8; (g) at pH value of 11.2. The insets show enlarged SEM images of ZnO NSs (scale bar = 100 nm).

FIGURE 3: Cross-sectional SEM image of the ZnO NRs grown under conditions $T = 90^{\circ}\text{C}$, $t = 6$ hrs, $\text{pH} = 6.6$, and $C = 100$ mM.

growth solution were adjusted to 1.8, 2.5, 3.5, 4.6, 6.6, 8, 9.2, 10.7, 11.2, and 12.5, respectively. Figure 1 represents the plot of the $\text{pH}_{\text{initial}}$ versus the final pH (pH_{final}) recorded over a period of 5 hrs using 100 mM precursors concentration. The experiments carried out in this range of pH (1.8–12.5) either with procedure A or procedure B showed that the alkaline pH was relatively decreased with the same rate, while the acidic pH was converged to 5.4 apparently approaching the inherent value 6.6. It is to mention that the same experiments have been repeated four times giving the same results, indicating the reproducibility of this process. To correlate the growth rate of the ZnO NSs with the pH, a set of samples were grown on the preseeded Si substrates with $T = 90^{\circ}\text{C}$ and $t = 5$ hrs in adjusted $\text{pH}_{\text{initial}}$ growth solutions. The inherent pH solution was transparent, and there were some visible white precipitates in the solution. The obtained NRs from the inherent pH solution have an average length of $2.2\ \mu\text{m}$ and diameter of 400 nm. The length was measured

FIGURE 4: SEM images of ZnO NSs on Si substrate with different precursor concentrations of the growth aqueous solution (a) at 25 mM; (b) 50 mM; (c) 100 mM; (d) 300 mM. Inset shows the magnified view of the ZnO NSs (scale bar = 100 nm).

from the cross-sectional SEM image (Figure 3) while the diameter was measured from the top view SEM as shown in Figure 2(d). Since in the inherent solution HMT was used as a precursor for the growth of ZnO NSs, first it hydrolyzes to produce the OH^- and ammonia. Then, the OH^- forms a complex with Zn^{2+} , followed by thermal decomposition into ZnO. The chemistry of the reaction during growth in the solution is discussed by Zainelabdin et al. [21]. When the pH was increased by adding $\text{NH}_3 \cdot \text{H}_2\text{O}$, the ammonia hydrolyzed into NH_4^+ and hydroxide giving rise at the same way to the increases of OH^- concentration in the solution. The following chemical reactions are governing the growth process:

Figure 2 shows the SEM images of various NSs grown under different initial pH values. Figure 2(d) shows high density NRs structure prepared from solution at $\text{pH}_{\text{initial}} = 6.6$ without $\text{NH}_3 \cdot \text{H}_2\text{O}$, indicating that at this OH^- concentration only rod-like structures can be grown. When the pH was increased to 8 nanotetrapod ZnO NSs were obtained as shown in Figure 2(e); this can be attributed to the hydroxide concentration increase in the initial solution, giving rise to the anisotropic growth directions. When we increased the pH to 9.1 the growth rate increased due to the increases of OH^- concentration which gives rise to ZnO particles in the solution. The resulting structure (Figure 2(f)) was a flower-like structure with thick arms. Figure 2(g) shows ZnO urchin-like structures with needles length of $2 \mu\text{m}$ and a diameter of $\sim 50 \text{ nm}$ for samples prepared from a solution with $\text{pH} = 11.2$. The inset shows high magnification image of ZnO nanoneedle. Similar surface morphology structures were obtained at pH of 12.5. We believe that by increasing the OH^- ions as compared to Zn^{2+} concentrations reaction (4) immediately starts to take place.

FIGURE 5: Plot of concentration versus average length and diameter of the ZnO NSs.

The $[\text{Zn}(\text{OH})_4]^{2-}$ acts as the new growth precursor while the nuclei obtained in reaction (3) serve as the seed. Therefore anisotropic growth of ZnO occurs at the active site of ZnO seed. Finally, we observed that for the high pH starting solution, the obtained structures were self-assembled.

By inspecting the cases for $\text{pH} < 7$ by adding either HNO_3 or HCl very different results were obtained. Figures 2(b) and 2(c) demonstrate the SEM images for the case with initial pH values of 1.8 and 4.6, respectively. The obtained structures were nanorods with hexagonal shape, the diameter and length were increased, and the density was largely decreased by the addition of HNO_3 or HCl or by lowering the pH values. The dissolution of precipitates occurs according to reaction (2). As the HNO_3 or HCl is added, more and more Zn^{2+} is formed and therefore the resulted ZnO nanorods grow to a larger length and diameter as shown in Figures 2(b) and 2(c). However, very large dimension rods were obtained at $\text{pH} < 4.6$ and down to 1.8 in the HNO_3 adjusted environment but they were eroded as clearly seen in the SEM image of Figure 2(a), and the etching was severe at the lowest pH values which also support the results that the ZnO starts to be etched in an acidic nature solution [22]. However, for $\text{pH} < 4.6$ no growth was obtained when the pH value was lowered by HCl . This can be due to the fact that the etching was dominating over the growth. It is also worthwhile to mention that after inspecting the SEM images of these samples there were no signs of a seed layer (ZnO nanoparticles) and the substrate was clean which shows that the etching was dominant.

3.2. Effect of the Precursor Concentration. In this section the concentration variation of the reactants using inherent pH value of 6.6 is discussed. It is well known that increasing or decreasing the concentration of the chemical reactants will eventually influence the resultant products. In the original paper which describes the growth of ZnO NRs via aqueous solutions, they have obtained microrods since a high concentration of the initial reactants was used [23]; when a relatively low concentration was used by the same authors the ZnO NRs were achieved [24]. This implies that a good control over the chemical reactants can be utilized

to gain direct control over the dimensions of the final ZnO NRs. According to this fact we have studied the effect of the reactants concentration on the dimensions of NRs as mentioned above starting by the inherent pH value. Scanning electron microscope images of ZnO NRs grown at different concentrations of the aqueous solution containing equimolar concentrations of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMT are shown in Figure 4; inset shows the magnified SEM image. The density, length, and diameter of the ZnO nano-/microrods are varied with the concentration applied during the synthesis; a higher concentration yields a micro-sized diameter with densely packed c-axis aligned ZnO rods as shown in Figure 4(d). Furthermore, for concentrations > 400 mM the microrod sized ZnO is converted into a polycrystalline thin film. On the other hand a low concentration (10 to 25 mM) of aqueous solution results in wire-like NRs with a diameter < 100 nm, and the length was found to be $1.2 \mu\text{m}$, evenly covering the substrate as revealed in Figures 4(a) and 4(b). Moreover, for concentrations less than 5 mM no growth was achieved on the substrate at the specified duration of 5 hrs, instead only residual ZnO was deposited on the bottom of the glass beaker suggesting that the longer time is required to grow ZnO NSs. When the growth was established for longer time (20 hrs) ultrathin NWs were achieved covering the substrate evenly. Nevertheless, Zhu et al. have synthesized ZnO-based core/shell structure at 5 mM at shorter time by modifying the aqueous solution [25]. The results of the precursor concentration variation with the ZnO NRs dimension are summarized in Figure 5. The graph clearly demonstrates that a linear relation can be drawn between the increase of the concentration and the NRs dimensions; interestingly the diameter of the NRs increases gradually, while the length becomes constant above 200 mM. This implies that there is a critical length for the ZnO NRs at which further increase of the concentration will not have any role in the axial growth direction whereas the radial direction grows continuously and at high enough concentration the rods merge to form continuous thin film.

3.3. Influence of the Growth Time. To investigate influence of the growth time on the ZnO NRs, we have grown the ZnO NRs in equimolar concentration (100 mM) of HMT and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at constant temperature of 90°C and inherent pH value of 6.6 for 1, 3, 6, 10, and 20 hrs. Figure 6 shows the cross-sectional SEM images of the ZnO NRs grown at different durations. It can be noticed from the figure that the growth duration is an important factor to control the size of the final ZnO structure. Figure 6(a) shows SEM image of ZnO NRs grown for a time of 1 hr, with an average length of 500 nm, indicating that rods are emerging on the nucleation sites. These embryonic NRs continue to grow with increasing the growth duration. When growth was conducted for 3 hrs average sized NRs with length of $1.0 \mu\text{m}$ were obtained (Figure 6(b)). By further increasing the growth time to 6 hrs the NRs length was boosted to $1.8 \mu\text{m}$ as revealed in Figure 6(c). The length has increased up to $2.2 \mu\text{m}$ when the growth time was increased to 10 hrs as seen in Figure 6(d), while no further increase of the ZnO NRs size was observed above 10 hrs. The inset in Figure 6 shows a top

FIGURE 6: Cross-sectional SEM images of ZnO NRs on Si substrate at different growth times: (a) 1 hr; (b) 3 hrs; (c) 6 hrs; (d) 10 hrs at $T = 90^\circ\text{C}$. The inset shows the corresponding top view of the SEM images.

FIGURE 7: Plot of ZnO NRs synthesis time versus change in average length and diameter.

view of the corresponding SEM images to the ones shown in the figure; here the diameter of the obtained ZnO NRs was changed from 150 nm to 500 nm with the change of time as stated above. Utilizing the cross-sectional and top view SEM images we calculated the lengths and diameters of ZnO NRs with growth time, and the result is summarized in Figure 7. The results indicated that continuous and steady growth of ZnO nanostructures precedes until the first 10 hrs and then the system would be in closure-precipitation equilibrium

stage as indicated in Figure 7. It is believed that with the passage of time the OH^- would continuously hydrolyze in the water solution from HMT up to 10 hrs then the OH^- would be consumed. The results show that the density of the ZnO nanostructures depends on the reaction time. The threshold time for growing ZnO NRs was observed to be one hour; therefore no growth was obtained below one hour.

3.4. Influence of the Growth Temperature. The effect of T on the ZnO NSs was also investigated. In our experiments, a set of samples were grown in the aqueous solution using a pH = 6.6, $t = 5$ hrs, and 100 mM precursors concentration in a controlled digital laboratory oven. Our growth temperature was changed from 50°C up to 110°C . The SEM images of this set of samples are shown in Figure 8. Figure 9 shows the plot of the aspect ratio of ZnO NRs versus T when the growth was performed in aqueous solution with an initial pH of 6.6. From these figures it can be seen that by changing T the aspect ratio is gradually increased up to 95°C . However, no further increase in the aspect ratio was observed at 110°C . The structure remained rodlike and the density was almost the same. Therefore, we believe that the size of the ZnO NSs can be controlled by changing T , and we suggest that the feasible T for the growth is $<100^\circ\text{C}$ since it is an aqueous based (water-based) solution. The crystallinity of the ZnO NRs grown at 90°C for 5 hrs and with a pH 6.6

FIGURE 8: SEM images of ZnO NRs on Si substrates for the growth temperatures (a) 50°C; (b) 70°C; (c) 90°C; (d) 110°C for 5 hrs and at 100 mM concentration. The inset is the magnified image (scale 100 nm) of single rod.

FIGURE 9: Plot of aspect ratio of ZnO NRs versus growth temperature (T) under the conditions of $C = 100$ mM, $t = 5$ hrs, and inherent pH.

was investigated by XRD as shown in Figure 10. The XRD pattern exhibited sharp diffraction peaks which correspond to ZnO wurtzite structure and agree well with the values available in the JCPDS 36-1451. From the above discussion

we can say that the pH controls the morphology and the precursor concentration controls the nucleation density, while the growth time controls the aspect ratio and finally the temperature control the aspect ratio and morphology. By

FIGURE 10: XRD pattern of ZnO NSs grown under the conditions of $T = 90^\circ\text{C}$, $t = 5$ hrs, and inherent pH.

adjusting these parameters, we can control the growth and obtain the desired ZnO NSs.

4. Conclusion

In conclusion, we studied the morphological control of ZnO nanostructures by adjusting possible parameters such as the pH, the concentration, the time, and the growth temperature. We have observed that the initial pH employed always changes during the growth, tending toward a neutral pH. Nanotetrapod-like, flower-like, and urchin-like ZnO nanostructures were obtained at higher pH values (≥ 8), while rod-like structures were obtained at lower pH. It was also noticed that the ZnO NRs were etched at a $\text{pH} \leq 4.6$. Furthermore, the precursor concentration, time, and temperature of growth were found to affect the morphology and dimensions of the ZnO nanostructures, changing from nanowires to nanorods and even to a film-like structure. We believe that the morphological and structural characteristics of the grown samples can be controlled by simply tuning the above-mentioned growth parameters to obtain the desired nanostructures as these experiments were reproducible.

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