Improved Ultraviolet Photoresponse Properties of ZnO Nanorods Grown by Using Hydrothermal Method Applied Rotating Precursor Solution

Dongwan Kim and Jae-Young Leem*

Department of Nanoscience & Engineering, Inje University, Gimhae 50834, Republic of Korea

Abstract: We grew ZnO nanorods (NRs) using a hydrothermal method while rotating the precursor solution, and report the effect of rotation on surface modification, and the optical and ultraviolet (UV) photoresponse properties of the resulting ZnO nanorods. The ZnO NRs grown in the rotating precursor solution at 100 rpm had the longest length and diameter, which decreased with increasing rotation rate above 100 rpm. Also, the intensity of the diffraction peaks from ZnO (002) and (100) was strongest and weakest for the ZnO NRs grown in a rotating solution at 150 rpm, respectively, indicating improvement in the c-axis orientation of the ZnO NRs. In the PL spectra, near-band-edge (NBE) and deep-level (DL) emissions were observed from all of the ZnO NRs. The intensity of the NBE emission gradually increased with increasing rotation rate, due to the increase in surface area. Also, the intensity of the DL emission gradually increased with increasing rotation rate because of the increasing number of interstitial oxygens. Analysis of the UV photoresponse found the photocurrent of the ZnO NRs grown in the rotating precursor solution was higher than that of ZnO NRs grown in a non-rotated precursor solution. In particular, ZnO NRs grown in a rotating precursor solution at 150 rpm exhibited the highest value of photosensitivity, with high reproducibility.

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1. Introduction

In the past several decades, one-dimensional (1D) nanostructures have attracted considerable attention due to their distinguishing features, including quantum-mechanical confinement effects and high surface-to-volume ratios, which have high value in a number of potential applications [1,2]. Among them, ZnO is one of the most interesting II-VI semiconductors because of its distinguishing characteristics, such as a wide direct bandgap (3.37 eV), exciton binding energy (60 meV), high thermal stability, and high electron mobility [3-5]. 1D ZnO nanostructures, such as nanorods (NRs), nanowires and nanobelts are particularly suitable nanostructures for UV photodetectors, because of their quantum-mechanical confinement effects and high surface-to-volume ratio [6-9]. For these reasons, ZnO are considered a promising material for efficient UV photodetectors and blue light-emitting devices. UV photodetectors have numerous practical applications in flame detection, environmental studies, and medical communication equipment [10,11]. However, before 1D ZnO NRs can be practically utilized in such photodetectors, their photoresponse properties (e.g., photoresponsivity and photosensitivity) must be improved. This involves improving the crystalline ZnO NRs. High-quality ZnO NRs can be prepared under high vacuum and high energy experimental conditions, using molecular beam epitaxy, thermal evaporation, and metal-organic chemical vapor deposition, however, such processing methods make them unacceptably expensive [12,13]. In contrast, the hydrothermal approach is a simple method for growing ZnO NRs. It provides a high deposition rate, easy dopant concentration control, and low growth temperature.

In the hydrothermal method, growth of the ZnO NRs is accomplished by combining Zn\(^{2+}\) and OH\(^-\) ions [14], and as a result, their growth rate is affected by the number of Zn\(^{2+}\) and OH\(^-\) ions. The number of Zn\(^{2+}\) ions in the precursor
solution is determined by the molarity of the precursor reagent, such as zinc nitrate hexahydrate. The number of OH ions can be controlled by the insertion of hexamethylenetetramine (HMT), the temperature of the precursor solution, and the insertion of ammonia solution to increase the pH value [15]. However, while an appropriate increase in pH will increase the number of OH\(^{-}\) ions, providing a fast growth rate, an excessive increase in pH accelerates the dissolution of already grown ZnO NRs and degrades their structural properties. Thus, to prevent the degradation of hydrothermally grown ZnO NRs, many researchers have used HMT as the source of OH\(^{-}\) ions. This also presents challenges, since the use of HMT causes a sharp transformation in the end of the ZnO NRs, which reduces their performance in a UV photodetector. Various methods have been used to prevent this problem, and surface modification has been found to be the most effective way to change their physical properties and improve performance in devices without undesirably transforming the end of the ZnO NRs.

Narayanan et al. reported that annealing hydrothermally grown ZnO NRs led to changes in their morphology, and improved their optical and electrical properties [16,17]. Also, Park et al. reported that using a rotating cathode for electrodeposition not only accelerated the supply of OH\(^{-}\) ions but also resulted in modification of the morphology of the ZnO NRs, improving their UV sensing properties [15]. However, point defects such as interstitial zinc and oxygen vacancies can also be generated by annealing ZnO NRs. At the same time, there have been few studies about the surface modification of ZnO NRs using the hydrothermal method.

In this study, we propose an effective and simple method to improve optical and photoresponse properties of ZnO NRs and modify their morphology. We grew the ZnO NRs using the hydrothermal method while rotating the precursor solution during the growth process. We then investigated changes in the structural and optical properties of the ZnO NRs according to the rotational speed of the precursor solution, as well as changes in the ZnO NRs morphology. We then fabricated UV photodetectors based on the ZnO NRs to observe changes in the UV photosresponse depending on the rotation rate of the precursor solution.

2. Experimental Procedures

We grew the ZnO NRs using a hydrothermal method with a rotating precursor solution to observe the effect of rotation rate on the ZnO NRs. The growth method consisted of two processes: deposition of a ZnO seed layer and growth of the ZnO NRs. The ZnO seed layer was deposited on a Si substrate using a sol-gel spin-coating method. To prepare the sol-gel solution, we dissolved zinc acetate dihydrate ([C\(_6\)H\(_5\)O\(_2\)Zn\(\cdot\)2H\(_2\)O] guaranteed reagent, ≥99.0%, JUNSEI) and monoethanolamine (MEA) ([NH\(_2\)CH\(_2\)CH\(_2\)OH], ACS reagent, ≥99.0%, Sigma-Aldrich) in 2-methoxyethanol ([C\(_3\)H\(_6\)O\(_2\)]), guaranteed reagent, ≥99.0%, JUNSEI). The zinc acetate/MEA molar ratio was 1:1 and the concentration of the ZnO precursor solution was 0.5 M. The mixture was stirred at 60 °C for 2 h to yield a clear and homogeneous solution, which then served as the coating source after being cooled down to room temperature. The Si substrates were cleaned in a piranha solution which was made by mixing sulfuric acid ([H\(_2\)SO\(_4\]), guaranteed reagent, ≥99.5%, Junsei) and hydrogen peroxide ([H\(_2\)O\(_2\)], guaranteed reagent, 30%, Junsei) and subsequently in hydrofluoric acid ([HF], guaranteed reagent, 48%, Junsei). Then, the cleaned substrates were rinsed with deionized water for 2 min and dried with nitrogen (N\(_2\)) gas (99.99999%). Then, the Si substrates were cleaned by ultrasonication in acetone ([CH\(_3\)COCH\(_3\)], ACS reagent, 99.5%, Sigma-Aldrich) and ethyl alcohol ([C\(_2\)H\(_5\)OH], guaranteed reagent, 99.9%, Junsei) for 10 min, rinsed with distilled water for 2 min, and dried with N\(_2\) gas (99.9999%).

The ZnO seed layer was prepared using the sol-gel spin-coating on the Si substrates at 2000 rpm for 20 s. The spin-coated ZnO seed layers were preheated at 200 °C for 10 min. The spin-coating and preheating process of the ZnO seed layer was repeated three times, and the prepared ZnO seed layer was annealed at 700 °C for 1 h in a furnace.

To grow ZnO NRs on the ZnO seed layer, a precursor solution was prepared by mixing zinc nitrate hexahydrate ([Zn(NO\(_3\))\(_2\)·6H\(_2\)O], guaranteed reagent, ≥98.0%, Sigma-Aldrich) and hexamethylenetetramine (HMT) ([C\(_6\)H\(_5\)]\(_2\)N\(_2\)], ACS reagent, ≥98.0%, Sigma-Aldrich). The concentration of the precursor solution was 0.025 M. The ZnO seed layer was fixed in a Teflon-lined autoclave filled with prepared precursor
Dongwan Kim and Jae-Young Leem

solution. A magnetic stirring bar, which was included in the autoclave, was rotated at speeds of 100, 150, and 200 rpm during the growth period to rotate the precursor solution, and growth was proceeded at 140 °C for 4 h. Figure 1 shows a schematic illustration of the hydrothermal synthesis equipment with the rotating precursor solution.

After growth was completed, the ZnO nanorods were rinsed with deionized water and dried with high-purity N₂ gas. The surface morphology of the hydrothermally grown ZnO NRs was observed using field emission scanning electron microscopy (FE-SEM), and the structural properties of the ZnO NRs were obtained by X-ray diffraction (XRD), using a Cu-Kα radiation source (λ = 0.15406 nm) at an accelerating voltage of 40 kV. The optical properties of the hydrothermally grown ZnO NRs were measured using a photoluminescence (PL) system composed of a He-Cd laser with an excitation power of 20 mW and a 0.75 m single-grating monochromator with a photomultiplier tube. In addition, changes in the photoresponse properties of the ZnO nanorods due to the step-annealing were measured using a 365 nm UV source with a power density of 10 mW/cm² at a bias voltage of 1 V.

3. Results and Discussion

To observe how the rotation rate of the precursor solution affected the morphology of the ZnO NRs, we measured the surface of the ZnO NRs using FE-SEM, and the results of these measurement are shown in Fig. 2. The ZnO NRs grown in the non-rotating precursor solution had higher density than the other ZnO NRs grown in the rotating precursor solution. Also the ZnO NRs grown in the non-rotating precursor solution had a length of 1.85 μm and a diameter of 76.3 nm. The lengths of the ZnO NRs grown in the rotating precursor solution at 100, 150, and 200 rpm were 3.62, 2.42, and 2.11 μm, respectively, indicating the length decreased with increasing rotation rate. Similarly, the diameter of the ZnO NRs decreased from 91.6 to 57.2 nm with increasing rotation rate. These results indicate that an appropriate rotation rate of precursor solution stimulated the generation of OH⁻ ions, and while excessively fast rotation rate also stimulated the generation of OH⁻ ions, it interrupted the formation of ZnO nuclei on the surface of the ZnO seed layer. The reduced quantity of ZnO nuclei caused the decrease in the length and diameter of the ZnO NRs with increasing rotation rate. Consequently, ZnO NRs grown in a rotating solution at an appropriate rotation rate, 100 rpm, had the longest length and diameter, while ZnO NRs grown in a
solution rotating at 200 rpm, which was relatively fast, had the shortest length and diameter.

The changes in the diameter and length of the ZnO NRs with increasing rotation rate can be also explained by the growth mechanism of the ZnO NRs. The growth of ZnO NRs in the hydrothermal method can be described by the following [18]:

\[
\begin{align*}
  \text{C}_6\text{H}_{12}\text{N}_4^++6\text{H}_2\text{O} & \Leftrightarrow 6\text{CH}_2\text{O} + 4\text{NH}_3  \\
  \text{Zn(NO}_3\text{)}_2 + 2\text{H}_2\text{O} & \Leftrightarrow \text{Zn(OH)}_2 + 2\text{HNO}_3  \\
  \text{Zn(OH)}_2 & \Leftrightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

The ZnO NRs are synthesized by the combination of Zn²⁺ and OH⁻ ions which are generated by zinc nitrate hexahydrate and HMT. When the Zn²⁺ and OH⁻ ions are generated in the aqueous solution, ZnO nuclei are generated on the ZnO seed layer. Since the ZnO nanorods grow by combining Zn²⁺ and OH⁻ ions, their growth is determined by the number of available ions. In our study, the number of Zn²⁺ ions was limited because the molarity of zinc nitrate hexahydrate was kept at 0.025 M. The number of OH⁻ ions was not limited.

Park et al. reported that rotating the cathode can stimulate the generation of OH⁻ ions and the resulting higher number of OH⁻ ions in the precursor solution increased the growth rate of ZnO NRs [17]. In this study, to observe changes in the number of OH⁻ ions, we measured the pH value of the precursor solution during the growth of the ZnO NRs. The results of the measurements are shown in Fig. 3. Before growth occurred, the pH value of all of the precursor solutions was kept as 6.3, for exact comparison. In the early growth stage (to 300 s), the pH value of the non-rotating precursor solution decreased, from 6.3 to 6.38, while the pH value of the non-rotating precursor solution decreased, from 6.3 to 6.18. Also, the average pH value of the rotating precursor solution was higher than that of non-rotated precursor solution. This was due to the increase in the number of OH⁻ ions in the rotated solution. This increase in OH⁻ ions continued until the end of growth. As a result, the rotation of the precursor solution stimulated the generation of OH⁻ ions, and the number of generated OH⁻ ions increased with increasing rotation rate.

The log scale XRD patterns of ZnO NRs which were grown in the rotating precursor solution using the hydrothermal method are shown in Fig. 4(a) and the intensity of the diffraction peaks from the ZnO (100) and (002) planes are also shown in Fig. 4(b). All the ZnO NRs had a strong intensity of diffraction peaks at 34.43° corresponding to diffraction from the ZnO (002) plane, and two relatively weak intensities of diffraction peak at 31.78° and 36.27° corresponding to the XRD peaks from the ZnO (100) and (101) planes, respectively, indicating the wurtzite structure of the hydrothermally grown ZnO NRs [19]. The intensity of the diffraction peak from the ZnO (002) plane of the ZnO NRs grown in the rotating precursor solution was stronger than that of the ZnO NRs grown in the non-rotating precursor solution. Notably, as shown in Fig. 4(b), the intensity of the diffraction peak from the ZnO (002) plane of the ZnO NRs grown in a solution rotating at 100 rpm, is weaker than that of the ZnO NRs grown in a solution rotating at 150 rpm. Also, the intensity of the ZnO (100) peak of the ZnO NRs grown in the solution rotating at 100 rpm is stronger than that of ZnO NRs grown in a solution rotating at 150 rpm. In general, the intensity of diffraction from the ZnO NRs is affected by the length and growth orientation of the ZnO NRs. The ZnO NRs grown in the rotating precursor solution at 100 rpm had longer length those than grown in the rotating precursor solution at 150 rpm, indicating that it was the growth orientation of the ZnO NRs that affected the intensity.
of the diffraction peak, rather than length of the NRs. This suggests the ZnO NRs grown in the rotating precursor solutions at 100, 150, 200 rpm were grown along the direction perpendicular to the substrate and, especially, the ZnO NRs grown in the rotating precursor solution at 150 rpm had a higher c-axis orientation than the other ZnO NRs.

Figure 5(a) shows the PL spectra of the ZnO NRs grown in the rotating precursor solution at 0, 100, 150, and 200 rpm, and Figure 5(b) shows the changes in the intensity of the near-band-edge (NBE) and deep level (DL) emissions with increasing precursor solution rotation rate. Typically, the PL spectrum of ZnO NRs contains NBE emissions and DL emissions, which can be observed in the UV and visible regions, respectively. It has been reported that the origin of the NBE and DL emissions in ZnO nanorods can be attributed to the recombination of free excitons, and defects such as oxygen vacancies, interstitial oxygens, zinc vacancies, and interstitial zinc, respectively [20]. The intensity of NBE emissions increased as the rotation rate of the precursor solution increased from 0 to 200 rpm. As mentioned above, the NBE emission of ZnO NRs is attributed to the recombination of free excitons. When photons are absorbed, electron-hole pairs are generated in the conduction and valence bands, respectively, because the absorbed energy of the photons is equal to or bigger than the band gap of the ZnO. But the generated electrons and holes have a short lifetime and recombine with each other. This recombination is defined as exciton recombination. The
The intensity of NBE emissions is determined by the amount of absorbed photons and generated electron-hole pairs [21]. The ZnO NRs grown in the non-rotating precursor solutions and those rotated at 100 and 150 rpm exhibited higher density of ZnO NRs than those grown in precursor solution rotating at 200 rpm. The relatively higher density of ZnO NRs grown in the non-rotating and rotating precursor solutions at 100 and 150 rpm caused a decrease in surface area where photons can be absorbed, due to interference and overlap of the ZnO NRs, as shown in Fig. 2(e)-(h). In contrast, the relatively low density ZnO NRs grown in the rotating precursor solution at 200 rpm had the largest surface area, because they had less interference and overlap. As a result, the ZnO NRs grown at 200 rpm exhibited a higher intensity of NBE emissions because a greater amount of photons were absorbed by the larger surface area, compared to the ZnO NRs grown in non-rotating precursor solution and those rotating at 100 and 150 rpm. Furthermore, the intensity of the broad yellow emission was increased nearly twice by rotation. It increased gradually as the rotation rate increased from 100 to 150 rpm, and decreased from 150 to 200 rpm. As mentioned above, the appropriate rotation rate, 100 to 150, stimulates the generation of OH\textsuperscript{-} ions, which increases the number of interstitial oxygens, while the excessively fast rotation rate restrains diffusion into the ZnO lattice in spite of producing a greater amount of OH\textsuperscript{-} ions. As a result, the ZnO NRs grown in the rotating precursor solution at 150 rpm exhibited the strongest DL emission intensity, and the ZnO NRs grown in the non-rotating precursor solution exhibited the lowest DL emission intensity.

To measure the UV photoresponse of the ZnO NRs according to rotation rate, metal-semiconductor-metal UV photodetectors were fabricated using the ZnO NRs. As shown in Fig. 6, the ZnO NRs grown in the rotating precursor solution at 100, 150, and 200 rpm exhibited higher photocurrent values than ZnO NRs grown in the non-rotating precursor solution. The photocurrent was affected by the number of free electrons in the ZnO NRs, which combined with oxygen atoms and generated oxygen ions [22]. The ZnO NRs grown in the rotating precursor solution had a greater amount of interstitial oxygen, which provided the free electrons, than ZnO NRs grown in the non-rotating precursor solution. The greater amount of free electrons resulted in more adsorbed oxygen ions, and increased the number of photo-generated electrons moving to the electrode with a bias voltage. Consequently, the ZnO NRs grown in the rotating precursor solution, which had a greater number of free electrons, exhibited higher photocurrents than ZnO NRs grown in the non-rotating precursor solution. We calculated the photosensitivity of ZnO NRs with
increasing rotation rate and the results are shown in Fig. 6(b). The photosensitivity of ZnO NRs can be calculated with the following equation [23]:

\[ S = \frac{I_{ph}}{I_{dark}} \]

where \( S \) is the photosensitivity of the ZnO thin films, \( I_{ph} \) is the photocurrent, and \( I_{dark} \) is the dark current. The calculated photosensitivity of the ZnO NRs gradually increased with increasing rotation rate from 0 to 150 rpm and decreased with increasing rotation rate from 150 to 200 rpm. This indicates that the ZnO NRs grown in a rotating precursor solution at 150 rpm generated the greatest amount of photo-generated electrons under the same intensity of UV light, and it is suitable for application in photodetectors, with high sensitivity and reproducibility.

4. Conclusions

We grew ZnO NRs using a hydrothermal method while rotating the precursor solution, and studied the effect of the rotation rate of the precursor solution on the morphological, optical, and photoresponse properties of the resulting ZnO NRs. The length of the ZnO NRs grown in non-rotating precursor solution was 1.85 μm, with a diameter of 76.3 nm. The length and diameter of the ZnO NRs decreased from 3.62 to 2.11 μm and from 91.6 to 57.2 nm when the rotation rate of the precursor solution was increased from 100 to 200 rpm. In the PL spectra, ZnO NRs grown in non-rotating precursor solution exhibited the lowest intensity of NBE and DL emissions. The ZnO NRs grown in the rotating precursor solution at 200 rpm exhibited the highest intensity of NBE emission and a lower intensity of DL emission than ZnO NRs grown in precursor solutions rotating at 100 and 150 rpm. The increase in NBE emissions was due to an increase in surface area. The increase in DL emission occurred because the rotation rate from 100 to 150 rpm stimulated the generation of OH- ions. An excessively fast rotation rate like 200 rpm, although generating a greater amount of OH- ions, restrained diffusion into the ZnO lattice. The results of the photoresponse measurements indicated the ZnO NRs grown in the rotating precursor solution had the higher value of photocurrent than ZnO NRs grown the non-rotating precursor solution, due to a greater amount of interstitial oxygen. The ZnO NRs grown in the rotating precursor solution at 150 rpm exhibited the highest photosensitivity. As a result, it can be concluded that rotating the precursor solution at an appropriate rate during growth is a suitable method of controlling the structural and optical properties of ZnO NRs, and improve their photosensitivity for application in UV photodetectors.

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