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# A novel growth method for ZnO nanorods by hydrothermal method applied rotating precursor solution

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In the last two decades, one-dimensional (1D) nanostructures have been extensively studied due to their distinguishing features such as quantum-mechanical confinement effects and high surface-to-volume ratios, exhibiting a number of potential applications. Of these, ZnO is one of the most interesting II-VI semiconductors with a wide direct bandgap of 3.37 eV and a high exciton binding energy of 60 meV at room temperature. In particular, ZnO can be excited to generate electron-hole pairs by absorption of ultraviolet (UV) light, being therefore regarded as promising material for efficient UV sensors and blue light-emitting devices, with the former finding numerous practical applications in fields such as flame detection, environmental studies, and medical communication equipment. However, the use of 1D ZnO NRs in such sensors requires their photoresponse properties (e.g., photoresponsivity and photosensitivity) to be improved. Threfore, to use the ZnO NRs in the sensor, it is necessary to improved crystalline ZnO NRs. The high-quality ZnO NRs can be prepared under high vacuum and high energy experimental conditions, such as molcular beam epitaxy, thermal evaporation, and metal-organic chemical vapor deposition, which, however, makes them unacceptably expensive. On the other hand, hydrothermal method is a simple method for the growth of ZnO NRs with a high deposition rate, ready control of the dopant concentration, and growth at low temperature and the growth of ZnO NRs through hydrothermal method is accomplished by the combination of Zn2+ and OH- ions. In other words, the growth rate of ZnO NRs through hydrothermal method is affected by the number of the Zn2+ and OH- ions. The number of the Zn2+ ions in the precursor solution is decided the molarity of precursor reagent like zinc nitrate hexahydrate, and the number of the OH- ions can be controlled by insertion of hexamethylenetetramine (HMT), temperature of precursor solution, and insertion of ammonia solution to increase value of pH. But, the appropriate increase of value of pH increases the OH- ions, which causes the fast growth rate of hydrothermal method, whereas the excessive increase of pH accelerates the dissolution of grown ZnO NRs and it causes the degradation of structural properties of ZnO NRs. Thus, to prevent the degradation of hydrothermally grown ZnO NRs, many researchers have used the HMT as the source of OH- ions. But, the use of the HMT causes the transformation of the end of ZnO NRs sharply, which decreased the performance of ZnO NRs-based UV detectors. Therefore, it is necessary to develop the new method for the improvement of declined structural and optical properties owing to the use of HMT as OH- ions source. Surface modification is one of the widely used methods to change the physical properties of different one-dimensional nanostructures for better performances of devices. Narayanan et al. reported that the annealing of hydrothermally grown ZnO NRs leads to changes of morphology of ZnO NRs, and it improves the optical and electrical properties of ZnO NRs. Also, Park et al. reported that the rotating cathode on the electrodeposition accelerates not only the supply of OH- ions but also modification of the morphology of ZnO NRs, which causes the improvement of UV sensing properties of ZnO NRs. However, the point defect such as interstitial zinc and oxygen vacancies can be generated by annealing of ZnO NRs, and there is little study about surface modification of the ZnO NRs using the hydrothermal method. Here we report a new and simple method to improve optical and photoresponse properties of ZnO NRs. We grew the ZnO NRs using the hydrothermal method with rotation of precursor solution and the precursor solution was rotated during the growth process. Also, we investigated the effect of rotation rate of precursor solution on the morphological, structural, and optical properties of the NRs, and fabricated the UV photodetectors based on the ZnO NRs to observe

the changes in the UV photoresponse with rotation rate of precursor solution. In FE-SEM images, the ZnO NRs grown at the non-rotated precursor solution had higher density than the other ZnO NRs grown at the rotating precursor solution. Also, in case of the ZnO NRs grown at non-rotated precursor solution, the length was 1.85 μm and the diameter is 76.3 nm. Furthermore, the length of ZnO NRs grown in rotating precursor solution at 100, 150, and 200 rpm was 3.62, 2.42, and 2.11 μm, respectively, indicating the decrease of length with increasing rotation rate. Similarly, the diameter of ZnO NRs, which grown in the rotating solution at 100, 150, and 200 rpm, decreased from 91.6 to 57.2 nm with increasing rotation rate. It is due to that the appropriate rotation rate of precursor solution stimulated the generation of OH- ions, whereas the excessively fast rotation rate interrupted the formation of ZnO nuclei on the surface of ZnO seed layer although it also stimulated the generation of OH- ions, and a small quantity of ZnO nuclei caused the decrease of growth rate of ZnO NRs. Therefore, ZnO NRs grown in a solution rotating at 100 rpm which is appropriate rotation rate had the longest length and diameter, whereas ZnO NRs grown in a solution rotating at 200 rpm which was relatively fast rotation rate had the shortest length and diameter. All ZnO NRs had a strong intensity of diffraction peaks at 34.43 o corresponded to the diffraction from ZnO (002) plane and two relatively weak intensities of diffraction peak at 31.78 o and 36.27 o corresponded to the diffraction from ZnO (100) and (101) planes, respectively. The Intensity of diffraction peak from ZnO (002) plane of ZnO NRs grown in rotating precursor solution was stronger than that of ZnO NRs grown at the non-rotated precursor solution. Especially, the intensity of ZnO (002) peak of ZnO NRs grown in a solution rotating at 100 rpm is weaker than that of ZnO NRs grown in a solution rotating at 150 rpm, while the intensity of ZnO (100) peak of ZnO NRs grown in a solution rotating at 100 rpm is stronger than that of ZnO NRs grown in a solution rotating at 150 rpm. In case of the PL spectra, the ZnO NRs grown in rotating precursor solution at 200 rpm exhibited the strongest intensity of NBE emission and it was due to that the ZnO NRs grown in rotating precursor solution at 200 rpm had the shortest length and diameter of NRs, indicating a greater amount of the photon absorption owing to the large surface area. Furthermore, the intensity of broad yellow emission increased about twice as the rotation of precursor solution occurred, and it gradually increased with increasing rotation rate of precursor solution from 100 to 150 rpm and decreased with increasing rotation rate of precursor solution from 150 to 200 rpm. As mentioned above, the appropriate rotation rate of precursor solution from 100 to 150 rpm stimulated the generation of OH- ions, which increased the number of interstitial oxygen, whereas the excessively fast rotation rate like 200 rpm retrained the diffusion into the ZnO lattice in spite of a greater amount of OH- ions. As a result, the ZnO NRs grown in rotating precursor solution at 150 rpm exhibited the strongest intensity of DL emission and the ZnO NRs grown at the non-rotated precursor solution exhibited the lowest intensity of DL emission. To measure the UV photoresponse property of the ZnO NRs with rotation rate of precursor solution, metal-semiconductor-metal UV photodetectors based on the ZnO NRs were fabricated. 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 at the non-rotated precursor solution. Thus, a greater amount of free electrons made a greater amount of adsorbed oxygen ions and it increased the number of photo-generated electrons moved to the electrode based on the bias voltage. Therefore, the ZnO NRs grown in the rotating precursor solution, which had a greater amount of free electrons, exhibited higher value of photocurrent than ZnO NRs grown at the non-rotated precursor solution. The photosensitivity of ZnO NRs can be calculated by the following equation:

S=I_ph/I_dark

where S is the photosensitivity of the ZnO thin films, Iph is the photocurrent, and Idark is the dark current. The calculated photosensitivity of ZnO NRs was gradually increased with increasing rotation rate from 0 to 150 rpm and decreased with increasing rotation rate from 150 to 200 rpm. It indicated that ZnO NRs grown in 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 photodetector with high sensitivity and reproducibility.

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