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Hydrothermally Grown ZnO Nanoflowers on a Template-Assisted Ordered Seed Array

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Abstract

1-D nanostructure arrays recently attract much attention because of their unique optical, structural, and electronic properties in the field of materials science, microelectronics, and optoelectronic engineering. Zinc Oxide (ZnO) nanoflowers were synthesized by a facile hydrothermal method on a template-assisted deposited ZnO seed array. The ZnO thin film was prepared via a sol-gel spin-coating process on a concave sapphire substrate first. Then an Al layer and an optically clear resin film were individually deposited on the ZnO thin film. After a lift-off process, a convex ZnO seed array film was formed. Finally, ZnO nanoflowers were synthesized by the hydrothermal method at 90^{o}C for 10 to 60 min. The structural, morphological and optical properties of the ZnO nanoflowers were investigated. The XRD results indicate that the ZnO nanoflowers were polycrystalline with a hexagonal wurtzite-type structure with a (002) preferential orientation. The FE-SEM micrographs exhibited the diameter and length of ZnO nanorods increased with the increasing growth time from 10 to 60 min. The 105-nm diameter and 1150-nm length nanorods were obtained with 60-min growth time. Photoluminescence spectra showed a sharp emission peak (I_{UV}) at approximately 380 nm and its intensity increased with the growth time. A weak emission band (I_{VIS}) at 450–550 nm was also observed and the I_{UV}/I_{VIS} increased with the growth time. This result indicates that the defects were reduced and the crystal quality was enhanced with the growth time. The prepared ZnO nanoflowers can be applied to various optoelectronic and sensing devices.

Keywords: zinc oxide, nanoflower, template-assisted, lift-off, hydrothermal, sol-gel

1. Introduction

Zinc Oxide (ZnO) is an II-VI compound semiconductor with a wide direct bandgap of 3.3 eV and a large exciton binding energy of 60 meV at room temperature. ZnO has the advantages of high thermal and chemical stability, easy processing by wet chemical etching and can be fabricated in various nanostructured forms and low-cost-low-temperature processes [1-2]. ZnO has been extensively used in fabricating transparent conducting electrodes, UV lasers and light-emitting diodes, solar cells, photodetectors, and gas sensors [3-7]. ZnO-based devices come out on the basis of bulk, thin film or nanostructured materials. Nanostructure materials are comprised of an array of zero-dimensional, one-dimensional (1-D), two-dimensional, and three-dimensional structures. Among them, 1-D nanostructure array materials generally have unique optical, structural, and electronic properties, and play an important role in the field of materials science, microelectronics, and optoelectronic engineering, especially for light harvesting and energy conversion/storage, environmental sensing and monitoring, and catalysis. The common representation of 1-D nanomaterials includes nanotubes, nanorods, nanowires, nanofibers, nanoflowers, etc. Nanoflowers are newly developed one of the nanomaterials that exhibit a structure similar to flowers. Because of its simple

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preparation method, high stability, and improved efficiency, it has attracted much attention [8]. [9] firstly proposed an organic-free hydrothermal process to prepare flower-like ZnO nanostructures in 2004. [10] presented that substrate played a crucial role in preparing ZnO nanostructures and the flower-like ZnO exhibited better optoelectronic performance than the block-like and rod-like ones. [11] reported that different concentrations of OH^- in the solution strongly affected the nucleation rate and crystal growth the morphology of flower-like ZnO. This work develops a novel approach to synthesize flower-like ZnO nanostructures on ordered seeded silicon substrates. Regardless of complicated equipment and expensive high-temperature vapor-phase methods, we adopt a low-cost aqueous chemical growth method, hydrothermal, to grow flower-like ZnO nanostructures, which are synthesized on the ordered ZnO seed arrays prepared via a template-assisted sol-gel spin-coating process. The structural, morphological and optical properties of the flower-like ZnO nanostructures were characterized.

2. Experimental Details

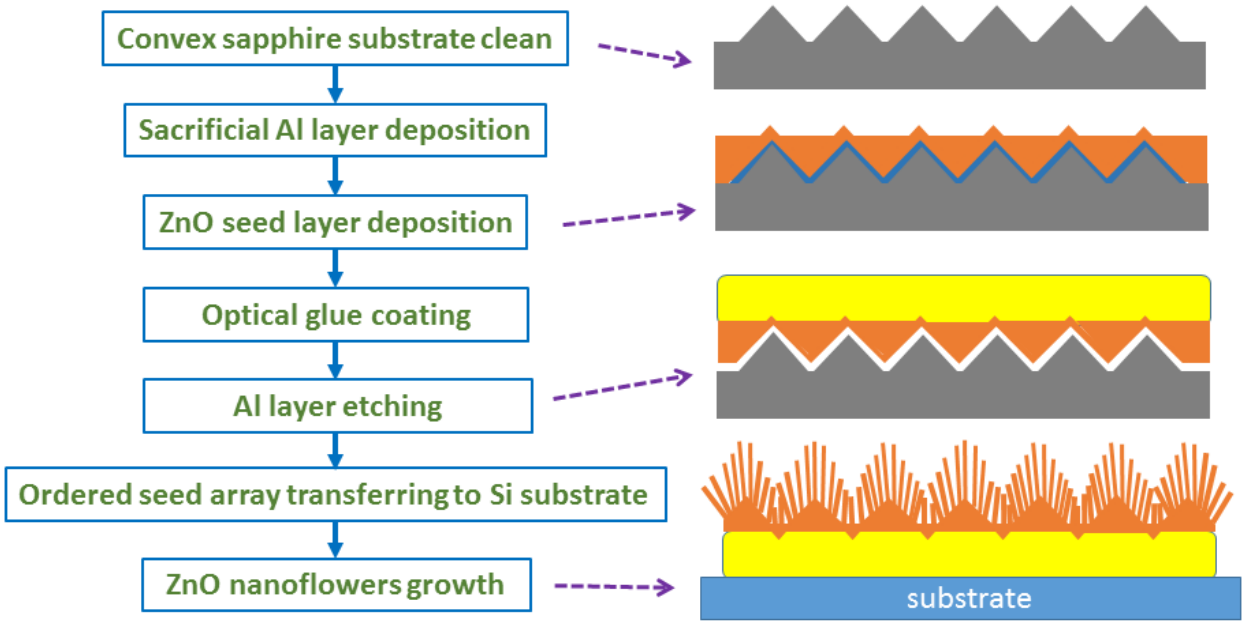
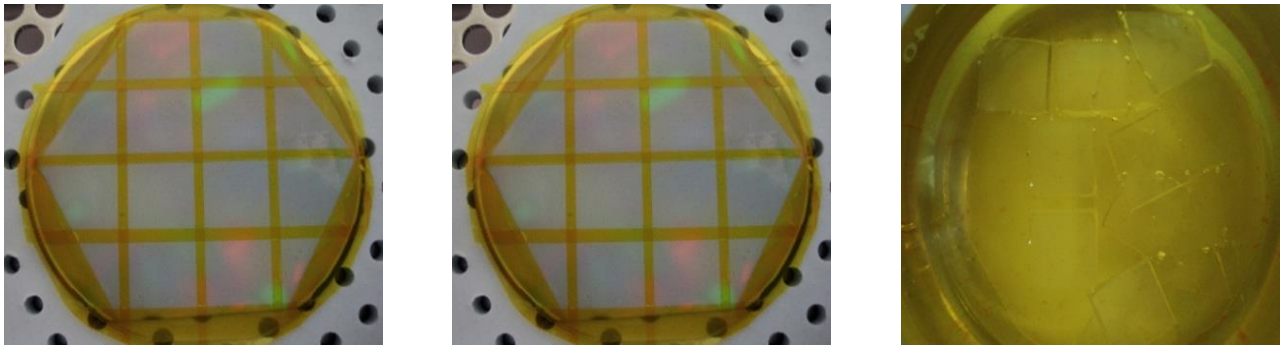


Fig. 1 Flowchart for the synthesis of ZnO nanoflowers

Zinc Oxide (ZnO) nanoflowers were synthesized by a facile hydrothermal method with a template-assisted deposited ZnO seed array. Fig. 1 shows the flowchart for the approach. The process consists of seven steps: (1) Concave sapphire substrates were cleaned with acetone, isopropyl alcohol, and D.I. water for 10 min each with an ultrasonic cleaner (Delta, DC-300) and then dried under nitrogen flow. (2) A sacrificial aluminum layer was deposited by thermal evaporation. (3) A ZnO seed layer with a thickness of approximately 190 nm was deposited via a sol-gel spin-coating process and then annealed in Ar ambient at 500℃ for 1 h. (4) An optical grade silicone A-B glue was coated and baked at 100℃ for 1 h, as Fig. 2 (a) shows. (5) The sacrificial aluminum was etched in a mixed solution with $K_3Fe(CN)_6$: KOH : H_2O = 10 g : 1 g : 100 ml. The etching rate was approximately 10 nm/s. Fig. 2 (b) and (c) exhibit the samples in the etching solution and after the etching process, separately. (6) The ZnO seed layer/silicone A-B glue was lift-off and transferred to silicon substrates. A convex ZnO seed array film was formed. (7) Finally, ZnO nanorods were synthesized by the hydrothermal method at 90°C for 10 to 60 min with the precursors of Zinc Acetate and Hexamethylenetetramine in D. I. water (200 ml). The structural, morphological and optical properties of the flower-like ZnO nanostructures were investigated by X-ray Diffraction (XRD) (PANalytical, 18-kW rotating anode X-ray generator, Japan) with Cu-Kα radiation (λ = 0.154056 nm) in θ–2θ scan mode, field emission scanning electron microscopy (FESEM) (3.0 kV; JEOL JSM-6700F, Japan), and Photoluminescence (PL) spectrometry (Horiba Jobin Yvon iHR550 fluorescence spectrometer) with a 325 nm He-Cd laser.

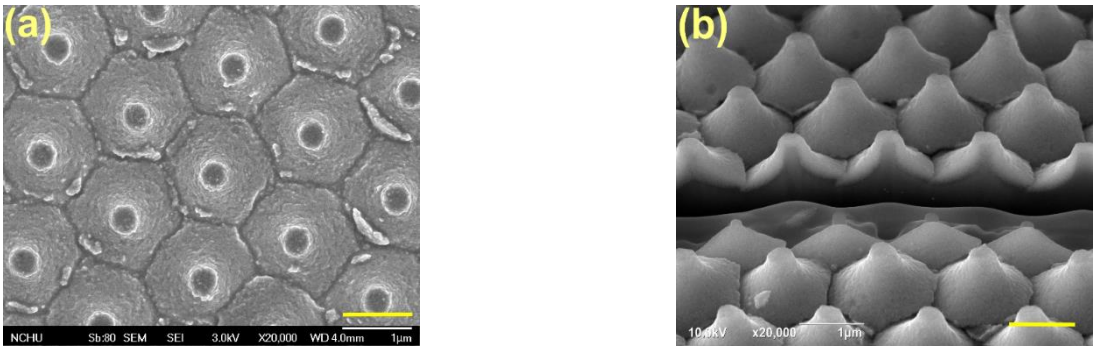


(a) after optical glue coating (b) in the etching solution (c) after the etching process

Fig. 2 Photographs of the samples

3. Results and Discussion

3.1. Characterization of ZnO seed array



(a) plan-view (b) 45° tilt view

Fig. 3 FESEM images of the ZnO seed film. The scale bar represents 1 μm.

Fig. 3 (a) and (b) shows plan-view and 45° tilt view FESEM images of the ZnO seed film on the concave substrates. From Fig. 3(a), it was found that the ZnO seed film formed a hexagonal pattern array and the pitch between the ZnO seed dots was about 1.35±0.2 nm. The surface particle size of the ZnO seed film was about 65±10 nm. From Fig. 3 (b), it was also found that the ZnO seed film exhibited a convex mountain-like array and the thickness of the ZnO seed film was 184 nm. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed and we found Si, Zn, O, and a small amount of Al and C elements on the samples. The appearance of Al may be caused by the deposition of aluminum impurities (such as aluminum hydroxide) in the etching solution for a long time. Fig. 4 shows XRD patterns of ZnO seed film on silicon substrates. The ZnO seed film has three weak diffraction peaks of (002), (100), and (101), and (002) orientation was slightly stronger than the others. This result suggests that ZnO seed film exhibits a wurtzite structure with polycrystalline structure.

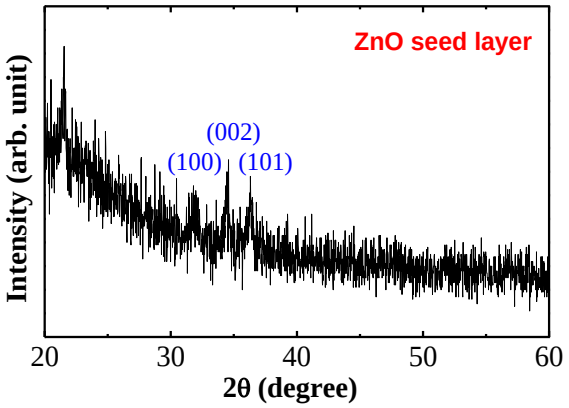


Fig. 4 XRD pattern of the ZnO seed film on silicon substrates

3.2. Characterization of flower-like ZnO nanorod array

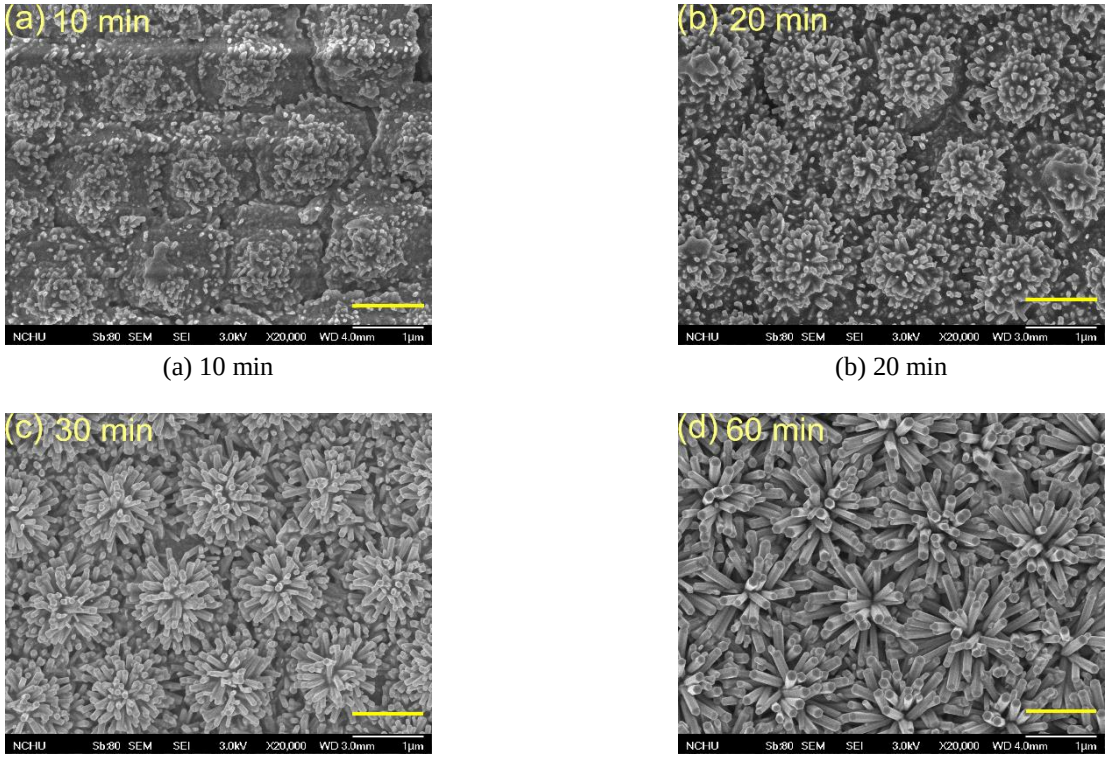


Fig. 5 Plan-view FESEM images of the flower-like ZNRA. The scale bar represents 1 μm.

Fig. 5 displays plan-view FESEM images of the flower-like ZnO nanorod array with the growth time (a) 10 min, (b) 20 min, (c) 30 min, and (d) 60 min. The length and diameter of the ZnO nanorods increased with the growth time from 10 to 60 min. The diameter of 105 nm of the ZnO nanorods was obtained for 60 min-growth times. For the sample with 10 min-growth times, the nanorods were short. It may be attributed to excess impurities on the seed film surface. Fig. 6 shows 45^{o} tilt-view FIB-SEM image of the flower-like ZnO nanorod array with a growth time of 60 min. The nanorod length was approximately 1125 nm after subtracting the thickness of the seed layer by 200 nm. The aspect ratio and density of the nanorods were calculated as 11.0 and 20 μm^{-2} for the sample with 60 min growth time.

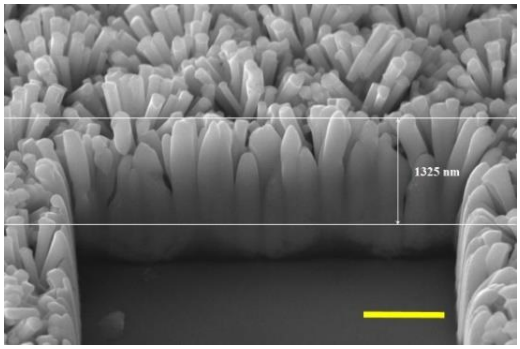


Fig. 6 45^{o} tilt-view FIB-SEM image of the ZNRA. The scale bar represents 1 μm

Fig. 7 shows XRD patterns of the flower-like ZnO Nanorod Array (ZNRA) grown by the hydrothermal method with growth times of 10, 20, 30, and 60 min. It was obvious that the intensities of the detected diffraction peaks increased with increasing growth time. Peaks with (002), (101), (102), (100), and (110) orientations were found, which suggests that the ZnO nanoflowers have a polycrystalline structure. The intensity of the diffraction peak in the (002) direction located at approximately 34˚was higher than the others, which indicates that the ZnO nanorods had a preferred orientation in the c-axis direction. This result conforms to the wurtzite structure of ZnO according to the JCPDS database. Fig. 8 shows

Photoluminescence (PL) spectra of the flower-like ZnO nanorods with growth times of 10 to 60 min. The PL spectrum showed that the relative intensity of Ultraviolet (UV) and visible light (450-550 nm) depends on the growth time of ZnO nanorods. The peak of photoluminescence of UV band approximately 380 nm was strongly enhanced when the growth time of ZnO nanorods was increased, while the visible bands decreased. The intensities of the UV band and visible band of PL spectra of the flower-like ZnO nanorods are listed in Table 1. The increase in UV intensity is related to the surface to volume ratios of the ZnO nanostructure, while visible luminescence (approximately 521-543 nm) caused by oxygen defects [12-13]. The decreased I_{VIS}/I_{UV} ratio with the increasing growth time indicates that the surface to volume ratio and crystal quality of ZnO nanorods can be enhanced by increasing the growth time. The calculated surface to volume ratio for the 60 min-sample was 3.90×10^{-2}. The improved crystal quality of the flower-like ZnO nanorod array consists of the result of XRD analysis.

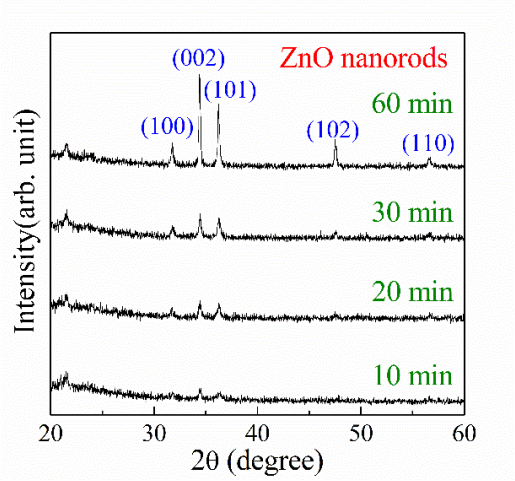


Fig. 7 XRD patterns of the ZNRA grown by the hydrothermal method

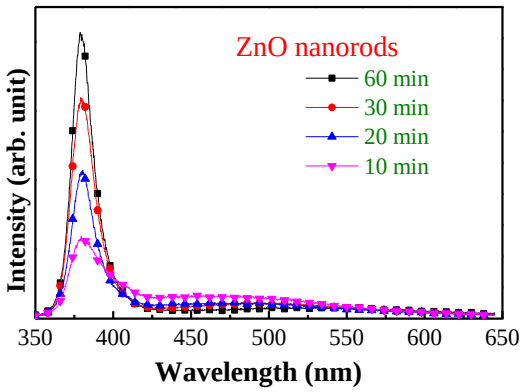


Fig. 8 Photoluminescence (PL) spectra of the flower-like ZNRA with growth times of 10-60 min

Table 1 Intensities of UV band and a visible band of PL spectra of the flower-like ZNRA with different growth times

Time	I_{UV}	I_{VIS}	I_{UV}/I_{VIS}
10	594.4	169.80	3.50
20	1073.6	118.61	9.05
30	1597.0	116.23	13.7
60	2068.4	83.22	24.9

4. Conclusions

The ZnO nanoflower array has been fabricated by a facile hydrothermal method via a template-assisted prepared convex ZnO seed array. The diameter and length of the flower-like ZnO nanorods both increased with increasing growth time. The diameter, length, aspect ratio, surface-to-volume ratio, and density of the ZnO nanorods were 105 nm, 1125 nm, 11.0,

3.90×10^{-2}, and 20 μm^{-2}, respectively, for the growth time of 60 min. The XRD analysis indicates that the ZnO nanoflowers were polycrystalline with a hexagonal wurtzite-type structure with a (002) preferential orientation. Photoluminescence spectra exhibited a strong UV peak at approximately 380 nm and a weak visible band (at approximately 450-550 nm). The increased I_{UV}/I_{VIS} ratio revealed that the defects were reduced and the crystal quality was enhanced with the increasing growth time. The developed ZnO nanoflowers array can be applied to various optoelectronic and sensing devices.

Conflicts of Interest

The authors declare no conflict of interest.

Acknowledgments

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