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Article

Growth of ZnO Nanoflower Arrays on a Patterned Sapphire Substrate

Ching-Shan Wang, Fang-Hsing Wang *, Han-Wen Liu

Department of Electrical Engineering and Graduate Institute of Optoelectronic Engineering, National Chung Hsing University, Taichung 402, Taiwan
* Correspondence: fansen@dragon.nchu.edu.tw

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Abstract: In this study, we investigated a novel technology to grow the ZnO nanoflower arrays on a patterned sapphire substrate using hydrothermal method. The process to prepare the substrate and grow ZnO nanoflower arrays were that the patterned concave sapphire substrates were cleaned using acetone, isopropyl alcohol, and D.I. water in an ultrasonic cleaner. Al sacrificial layer with the thickness of 600 nm was deposited using a thermal evaporation technology. The sol-gel process was used to deposit the ZnO seed layer on the patterned concave sapphire substrates, and then the ZnO seed layer was annealed at 500°C in Ar ambient for 1 h. The optical grade silicone A-B glue was coated on the ZnO seed layer and then the mixed solution of $K_3Fe(CN)_6$: KOH : H_2O = 10 g : 1 g : 100 ml was used to etch the sacrificial Al layer. (f) A lift-off technology was used to move the ZnO seed layer/silicone A-B glue to silicon substrate. Finally, a hydrothermal method was used to grow the ZnO nanorods on the ZnO seed layer/silicone A-B glue/silicon substrate at 90°C with the different durations of 10 to 60 min. Focused ion beam system (FIB) was used to observe the cross sectional morphology of patterned ZnO seed layer. The crystal structural of the flower-like ZnO nanostructures was analyzed using X-ray diffraction (XRD) pattern, the morphological of the flower-like ZnO nanostructures was observed using FIB and field emission scanning electron microscope (FESEM). Also, the optical properties of the flower-like ZnO nanostructures were investigated.

Keywords: ZnO-seed layer; Sacrificial layer; Hydrothermal method; ZnO nanoflower arrays; ZnO nanorods; Patterned sapphire substrate.

1. Introduction

The ZnO nanostructures including of hexagonal pyramid-like rods, microrods, whiskers, nanoribbons, nanowires, flower-like rod aggregates, and etc.. are successfully synthesized as different synthesis technologies are used [1-3]. Nanostructure zinc oxide (ZnO) materials attract remarkable attentions because they have some special and unique properties, and they can be applied in many nanodevices and nanosystems. For example, Kaur et al. used un-complicated hydrothermal method to grow the zinc oxide nanoflowers on glass substrate by controlling the pH value of the using precursor solution and investigated the ZnO-based nanoflowers as the piezoelectric nanogenerator [4]. Cheng et al. used the hydrothermal method to grow the ZnO nanocolumns on ZnO/ITO substrates, and the ZnO nanocolumns were used as the piezoelectric material to fabricate underwater hydrophones with different structures [5].

The mainly used methods of preparation ZnO-based one dimensional nanomaterials are the gas phase method and solution method, and the gas phase method can be divided into the vapor-liquid-solid (VLS) deposition method, chemical-vapor-deposition (CVD) method, metal-organic chemical vapor deposition (MOCVD) method, and zinc vapor oxidation method, etc. Solution method can be divided into the hydrothermal method, template-assisted growth method, electrochemical deposition method etc. For the template-assisted growth metho, there are many different materials are used as the templates, including polycarbonate (PC), porous anodic alumina membrane (AAM), polystyrene (PS) etc. When the one dimensional or two dimensional nanometerials can be obtained using the electroplating method, CVD method, and sol-gel method etc. to fill the growth materials into the holes, and the diameters of the holes in the templates are the diameters of the growth nanomaterials. When a hydrothermal method is used to synthesize the metal oxides, the precusours are the metal salts and the surfactant (for example, amine compounds) is added to control the growth pattern. After the solutions are heated, the solution becomes the oversaturation in a low saturation condition, the dissolution and condensation processes will cause the reactions of heterogeneous nucleation, then the metal oxide crystals are coprecipitation because of the oversaturation.

Hydrothermal method is a low-temperature synthesis technology, which can crystal the metal oxides at temperature below 100˚C and it can synthesize and grow the metal oxides in different morphologies by controlling the temperature, concentration, or pH value of the aqueous solution. Because when the synthesis parameters are changed, the solubility and supersaturation of precursor solution are changed and the crystal metal oxides are precipitated and formatted. Because the hydrothermal method can be processed at low temperature, as compared with the high temperature heat treatment process this method can significantly save process cost [5-8]. In this work, we proposed and investigated a novel technology to prepare the ZnO seed layer using a patterned sapphire substrate and synthesized the ZnO nanoflower arrays using the hydrothermal method under different synthesis time. After the patterned ZnO seed layer was prepared, the ion beam system (FIB) was used to observe its cross sectional morphology. The X-ray diffraction (XRD) pattern and the field emission scanning electron microscope (FESEM) were used to observe the surface morphologies and analyze the crystallization of growth ZnO nanoflower arrays. Also, a photoluminescence (PL) spectrometry was used to find the variations in the PL intensities of the ZnO nanoflower arrays.

2. Materials and Methods

In this study, a facile hydrothermal method was used to synthesize the zinc oxide (ZnO) nanoflower arrays using a template-assisted technology, which used patterned sapphire as the substrate. The process to prepare the substrate and grow ZnO nanoflower arrays consisted the following steps: (a) Acetone, isopropyl alcohol, and D.I. water were used to clean the patterned concave sapphire substrates, and each process time was 10 min in an ultrasonic cleaner (Delta, DC-300) and nitrogen flow was used to dry the patterned concave sapphire substrates. (b) Al was used as sacrificial layer to deposit on the patterned concave sapphire substrates, the sacrificial layer was deposited using a thermal evaporation technology and the thickness was about 600 nm by controlling the evaporation time. (c) The sol-gel process was achieved using spin-coating method to deposit the ZnO seed layer on the patterned concave sapphire substrates, the deposited ZnO seed layer had a thickness of approximately 190 nm by repeating the spin-coating process for six times. Next, the deposited ZnO seed layer was annealed at 500°C in Ar ambient for 1 h. (d) The optical grade silicone

A-B glue was coated on the ZnO seed layer and then they were baked at 100°C for 1 h. (e) After the A-B glue was backed, the mixed solution of $K_3Fe(CN)_6$: KOH : H_2O = 10 g : 1 g : 100 ml was used to etch the sacrificial Al layer, and the etching rate was approximately 10 nm/s. (f) A lift-off technology was used to move the ZnO seed layer/silicone A-B glue, and the ZnO seed layer/silicone A-B glue was transferred to silicon substrate. Then a convex ZnO seed array film with patterned matrix array was formed. (g) Finally, a hydrothermal method was used to grow the ZnO nanorods on the ZnO seed layer/silicone A-B glue/silicon substrate at 90oC with the different durations of 10 to 60 min. Zinc acetate and hexamethylenetetramine with a concentration of 0.2 M was used as the solution precursor in D. I. water. After the ZnO seed layer was prepared, we also used the focused ion beam (FIB) system to them for the observation of the cross sectional morphologies. The crystal structural of the flower-like ZnO nanostructures was analyzed as a function of growth time using X-ray diffraction (XRD) pattern, scanning in θ–2θ mode with Cu-Kα radiation of λ = 0.154056 nm; The surface and cross-sectional observations of the flower-like ZnO nanostructures were observed using FIB and field emission scanning electron microscope; The optical properties of the flower-like ZnO nanostructures were investigated at room temperature and in the wavelength range of 350~650 nm using a photoluminescence (PL) spectrometry, which used a 325 nm He- Cd laser as the exciting source. The schematic diagram of photoluminescence measurements is shown in Figure 1.

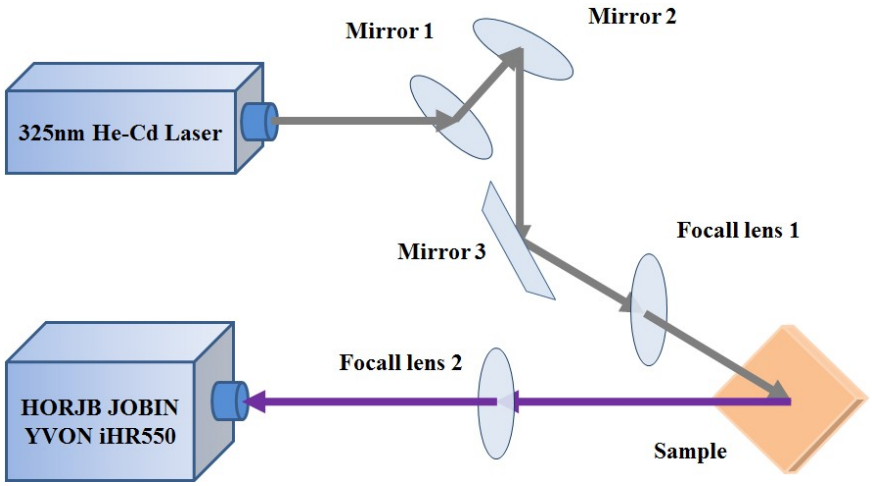

Figure 1. Schematic diagram of photoluminescence measurements.

3. Results

In this study, a thermal evaporation technology was used to deposit the sacrificial layer with the thickness of about 600 nm by controlling the evaporation time, and the prepared samples were abbreviated as SC. Figure 2 shows the surface mprphologies of etching results of sacrificial Al layer as a function of time. We used the heat-resistant tape to paste the etching channel on the ZnO seed layer deposited sapphire substrate, and the square area was 10 mmx10 mm, as the 0 hr in Figure 2 shows. From Figure we found that the area of sacrificial Al layer decreased with etching time, and when the etching time was 68 h, the sacrificial Al layer was etched completely.

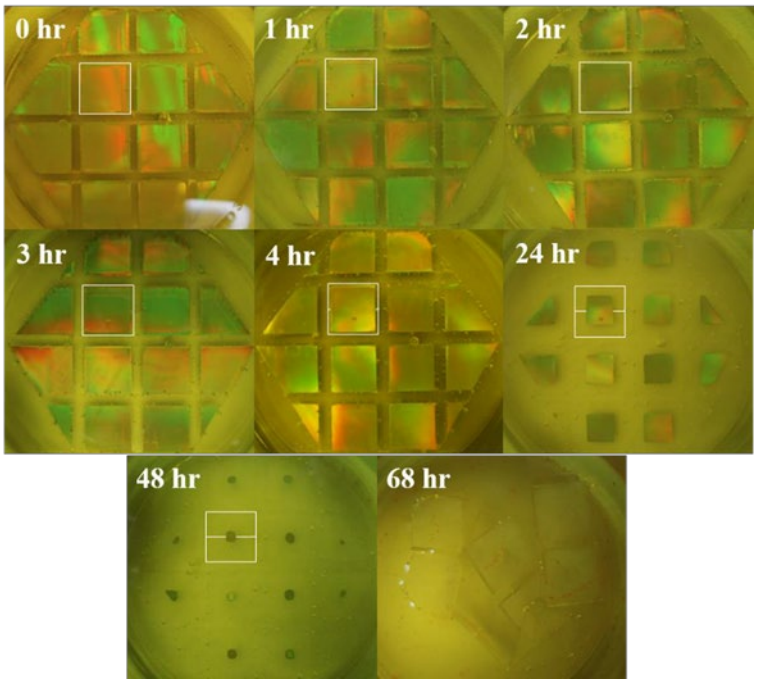

Figure 2. Etching results of sacrificial layer as a function etching time.

Figure 3(a) and Figure 3(b) show the surface morphologies of the ZnO seed layer under the observations of low magnification and high magnification. From the images we found that the average particle sizes of the ZnO seed layer was about 80 nm. Figure 3 (b) shows that the diameter of the top area of the ZnO seed layer was about 390 nm. The cross-sectional image of the ZnO seed layer is shown in Figure 3(c), the thickness was about 180 nm.

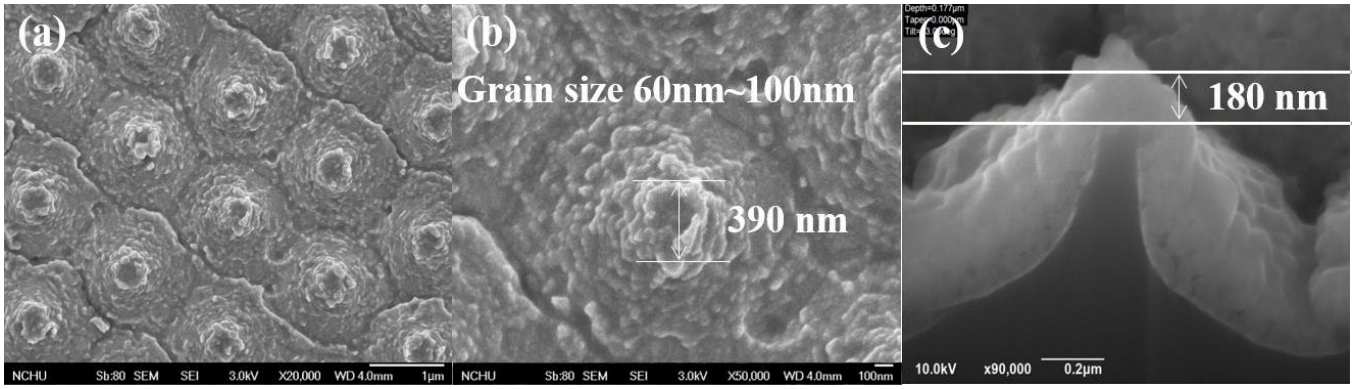

Figure. 3 SEM images of the templates at (a) low magnification and (b) high magnification, and (c) FIB cross-sectional view.

From the XRD pattern of the ZnO seed layer (not shown here) we found that the diffraction peaks located at 2θ values of 31.89˚, 34.59˚, 36.47˚, 47.63˚, and 56.77˚ were observed, which were corresponding to the diffraction direction peaks of (100), (002), (101), (102), and (110), respectively. XRD patterns of the grown ZnO nanoflower arrays as a function of growth time are compared in Figure 4, the concentration of the zinc acetate and hexamethylenetetramine was 0.2 M. The diffraction direction peaks of (100), (002), (101), (102), and (110) weer also observed,

and their diffraction intensities increased with growth time. As compared the diffraction results with the No.36-1451 of Joint Committee on Powder Diffraction Standards (JCPDS) Card we found that the ZnO- seed layer and the grown ZnO nanoflower arrays had the hexagonal close package (HCP) and a Wurtzite structure. Figure 4 also shows that the (002) was the strongest diffraction peak, which suggests that the ZnO-seed layer and the grown ZnO nanoflower arrays have the c-axis preferred orientation. The increase of diffraction intensities of (100), (002), (101), (102), and (110) peaks with growth time suggests that the crystallization of the grown ZnO nanoflower arrays increases with growth time. This result also suggests that the growth direction of the ZnO nanoflower arrays is not completely perpendicular to the surface of the substrate.

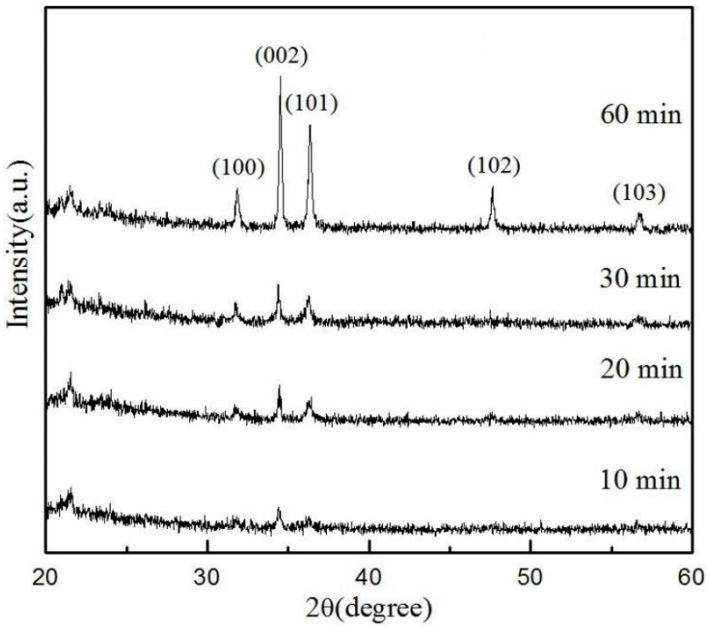

Figure. 4 XRD patterns of ZnO nanoflower arrays as a function of growth time.

The surface morphologies of the ZnO nanoflower arrays as a function of growth time are shown in Figure 5. As the growth time was 10 and 20 min, the diameter, the height, and the density (number of nanorods in the area of 1 μm^{-2}) could not be measured because the uniform ZnO nanorods were not grown, as Figure 5(a) and Figure 5(b) show. As the growth time was 30 and 60 min, the diameters were 88 and 120 nm, the heights were 623 and 975 nm, and the densities were 16.8 and 18 μm-2, as Figure 5(c) and Figure 5(d) show. These results prove that the growth time is an important factor to affect the diameter and the height of the ZnO nanoflower arrays, and we believe the growth time will also affect the PL properties of the growth ZnO nanoflower arrays.

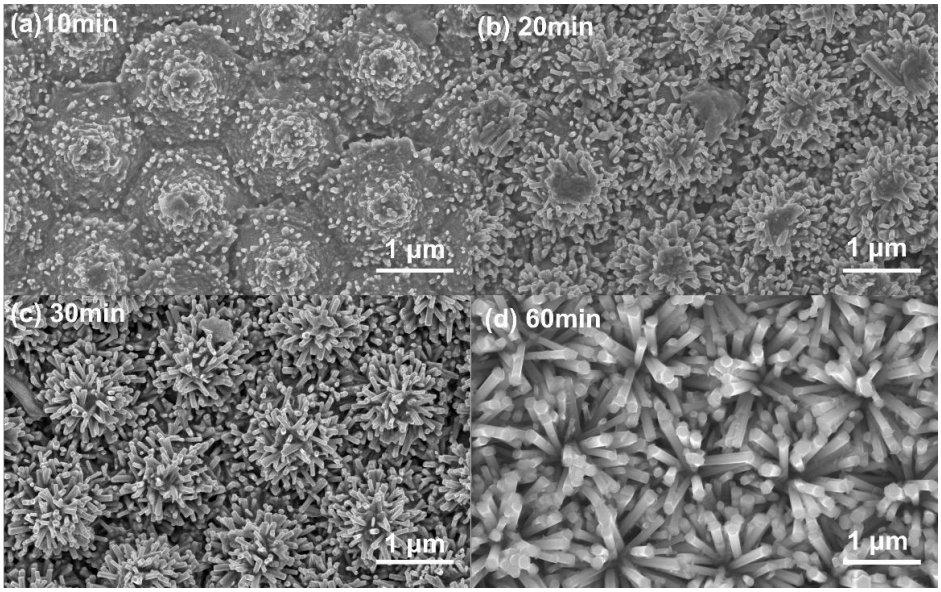

Figure. 5 Surface morphologies of ZnO nanoflower arrays as a function of growth time.

The PL spectra of the ZnO nanoflower arrays are shown in Figure 7as a function of growth time, and the exciting wavelength was 325 nm and this measurement was processed at room temperature. Figure 7 shows that as the growth time was 10, 20, and 30 min, two emission peaks located at 380 nm (UV emission) and 450~550 nm (visible emission) were presented; As the growth time was 60 min, the emission peak located at 380 nm (UV emission) and a weak emission located at 535 nm were observed. The broaden emission band located at 450~550 nm is recognized as the inducing by the Zn defect (about in the range of 405~427 nm) and oxygen defect (about in the range of 521~543 nm) [9]. The 380 nm (UV) emission in the PL spectra of the ZnO-based nanomaterials was recognized as the near-band-edge emission and the 450~550 nm (visible) emission band in the PL spectra of the ZnO-based nanomaterials was usually observed for most ZnO nanorods of the reported literatures, which was recognised to be caused by the defects of Zn interstitials, O vacancies, or their complexes [10]. However, the diffraction intensity for the peak at 380 nm increased and the diffraction intensity for the peak at 450~550 nm decreased with growth time. These results prove that as the growth temperature increases, the Zn defect and oxygen defect decrease. Table 1 compares the the maximum intensities of I_G and I_{UV} peaks and the variation of I_G/I_{UV} ratio of the ZnO nanoflower arrays as a fuction of growth time. As the table show, the I_G and I_G/I_{UV} ratio decrease with the growth time, which prove that the increase of growth time can decrease the defects and enhance the emission property of the ZnO nanoflower arrays.

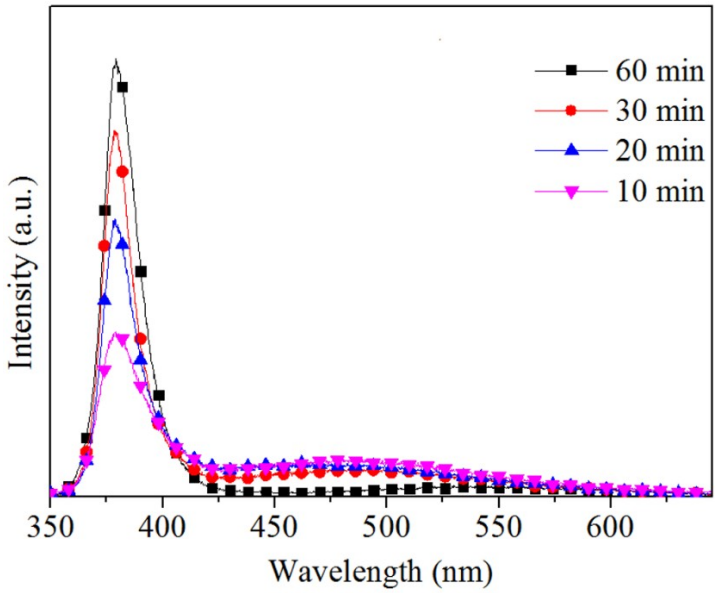

Figure. 6 PL spectra of ZnO nanoflower arrays as a function of growth time.

Table 1. Comparison of defect of ZnO nanoflower arrays as a function of growth time

Time (min)	I_{UV}	I_G	I_G/I_{UV}
10	580.81	144.82	0.249
20	971.15	126.50	0.130
30	1275.18	109.84	0.086
60	1522.18	48.72	0.032

4. Conclusions

We had successfully used the patterned sapphire substrate to prepare the ZnO seed layer and had successfully used the hydrothermal method to grow ZnO nanoflower arrays on the prepared ZnO seed layer. For the ZnO seed layer, its average particle size was about 80 nm, its diameter of the top area was about 390 nm, and its thickness was about 180 nm. From the XRD patterns of the ZnO seed layer and ZnO nanoflower arrays, the diffraction direction peaks of (100), (002), (101), (102), and (110) were observed. As the growth time of ZnO nanoflower arrays was 30 and 60 min, the diameters were 88 and 120 nm, the heights were 623 and 975 nm, and the densities were 16.8 and 18 μm-2, respectively. Two emission peaks located at 380 nm (UV emission) and

450~550 nm (visible emission) were presented in the PL spectra of the ZnO nanoflower arrays, and the diffraction intensity for the peak at 380 nm increased and the diffraction intensity for the peak at 450~550 nm decreased with growth time

Supplementary File: It is available online at www.iikii.com/afm/xxx/s001.

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Conflicts of Interest: The authors declare no conflict of interest.

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