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Effects of UV- Ozone treatment on Physical and Morphological Properties of Ga/F co-doped ZnO Nanostructures on ZnO Seed Layer

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Abstract

In this paper, we studied the modification surface wettability of ZnO seeding layer by UV-Ozone treatments for Ga/F co-doped ZnO (GFZO) nanostructures grown on ZnO seeding layer. The surface wettability is significant feature for growth of GFZO nanostructures by hydrothermal process. Good surface wettability can result to hydrophobic and hydrophilic properties that can be measured by water contact angle. The surface treatments of ZnO seeding layer were modified by UV-Ozone for different treatment time ranging from 0 to 20 min. The samples with treatment time of 0 and 2 min show the hydrophobicity with corresponding contact angle of 97° and 72°, respectively. The samples with longer treatment time from 4 to 20 min exhibit significant hydrophilicity with correlating contact angle of 38° and 17°, respectively. The results suggest that the smaller contact angles were obtained with longer treatment times. Moreover, the effects of UV-Ozone treatment on morphologies and structural of Ga/F co-doped ZnO nanostructures on ZnO seeding layer were investigated by X-ray diffraction (XRD) and Field emission scanning electron microscope (FE-SEM), respectively.

Keywords: UV-Ozone treatment, GFZO nanostructures, Surface wettability

1. Introduction

One-dimensional (1D) nanostructures have been extensively studied because of their potential applications in nanoelectronics-based devices. Specific synthesis of desired shape and size of nanomaterials with exceptional properties can lead to their appropriate applications. Nanostructures can be obtained by various growth techniques such as radio frequency magnetron sputtering [1], co-precipitation process [2], sol–gel process [3], and hydrothermal process [4]. Though several technologies have been established for the growth of a variety of nanostructures, hydrothermal growth technique is one of dominating and effective processes due to their low temperature processing, low cost, ease of equipment set-up, and environmental friendly aspect [5]. Therefore, 1D Zinc oxide (ZnO) nanostructures can be used for many applications, including ultraviolet light-emitting devices [6], chemical sensors [7], solar cells [8], and ultraviolet detector devices [9]. Typically, ZnO possesses a wide band gap (Eg~ 3.2-3.4 eV at 300 K), a large exciton binding energy (60 meV) and is n-type compound semiconductor [10]. ZnO has many advantages over other materials such as low cost, high stability and efficient excitonic emission [11]. Therefore, large effort has been devoted for considering the growth time, temperature and doping in order to control the structure and properties of ZnO nanostructures [12]. The electrical and optical properties of ZnO nanostructures can be considerably enhanced by suitable doping with both metal and non-metal elements such as

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would preferably substitute the Zn host atoms that could provide extra free electrons guiding greater conductivity or better carrier mobility. Among the metal dopants, Ga is considered to be a promising element due to its similar ionic radius (0.62Å) and covalent radius (1.26 Å) to those values of Zn (0.74 and 1.34 Å, respectively). The similar ionic radius would lead to lower lattice distortion, when doping, compared with Al, and In. Furthermore, the ionic radius of fluorine (0.117 nm) is similar to that of oxygen (0.122 nm) [13-15], fluorine may be a suitable anion doping candidate at oxygen site in Zinc oxide matrix. Furthermore, the seed layer is important in increasing the nucleation of nanostructure growth. The relationship between the nanostructure and the seed layer should be understood and clarified because the properties of Ga/F co-doped ZnO nanostructures highly depend on the properties of the ZnO seed layer, such as morphology, grain size, roughness, and crystalline density. Therefore, preparing a high-quality seed layer is significant step toward improving the performance of Ga/F co-doped ZnO nanostructure. In this work, we examine in a systematic way the influence of ZnO seeding layer treatment for growth of Ga/F co-doped ZnO nanostructures. The ZnO seeding layer treatment has been found to be one of the key factors that can control density and morphology of ZnO-based nanostructures by hydrothermal process [16-17].

2. Experimental details

The synthesis of GFZO nanostructures on ZnO seed layers coated on glass substrate consists of two steps. First, the ZnO seeding layer was deposited by dip-coating technique. The precursor solution used for dip coating was prepared by dissolution of zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$) and diethanolamine (DEA) in 100 ml absolute ethanol and was stirred until the precursor became clear. The precursor solution was then dip-coated onto cleaned glass substrates and annealed for 15 min at 100°C on a hot-plate and repeated for10 times. Finally, the coated films were annealed in a furnace at 500°C for 2 h to form ZnO seeding layer. Second, Ga/F co-doped ZnO (GFZO) nanostructures were synthesized by hydrothermal process. The solution for the synthesis of GFZO nanostructures was prepared by 100 mL of 0.05 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), gallium (III) nitrate hydrate (GaN_3O_9), ammonium fluoride (NH_4F) and hexamethylenetetramine (HMTA) into 50 mL deionized water. The desired concentration of gallium (III) nitrate hydrate and ammonium fluoride were fixed at 5% and 3%, respectively (designated as 5G3FZO). The seeding film layer were dipped into the prepared solution and loaded in a Teflon autoclave for the hydrothermal reaction operated at 90°C for 2 h. Finally, the obtained white solid product was separated from the solution by sonication, washed with distilled water, and dried at 100°C for 24 h. The crystal structures and morphologies of all samples were observed by XRD (Bruker D8 discover diffractometer) and Fe-SEM (Hitachi S-4700), respectively. The surface wettability of ZnO seeding layer was investigated by water contact angles measurement (model JYSP-360).

3. Results and discussion

Fig. 1. shows the contact angles between water droplets on glass and ZnO seed layers with various UV-Ozone times ranging from 0 to 20 min. The results between the water contact angle and UV-Ozone treatment showed that the smaller contact angles were obtained with longer treatment times. At 0 and 2 min of UV-Ozone treatment on ZnO seeding, the result showed the hydrophobic feature with a contact angle of 97° and 72°, respectively. After increasing treatment time at 4 to 20 min, the images exhibited the

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hydrophobic-hydrophilic conversion with a water contact angle of 38° to 17°, respectively. During UV-Ozone exposure, the system could continuously generate ozone and atomic oxygen. Moreover, the hydroxyl group and atomic oxygen may destroy the surface organic contaminants leading to the cleanliness and greater functional groups supporting the rod growth of the ZnO seeding layer surface. This surface modification reflects the change of hydrophobicity to hydrophilicity of the seeding layer surface. It could be further deduced that UV-Ozone treatment process is a crucial process for growth of GFZO nanostructures on ZnO seeding layer. Moreover, X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM) were conducted to investigate the effects of UV-Ozone treatment on morphologies and structural properties of GFZO nanostructures on ZnO seeding layer (shown in Fig. 2. and Fig. 3.). Fig. 2 shows the X-ray diffraction patterns of GFZO nanostructures grown on ZnO seeding layers modified by UV-Ozone treatment. XRD results indicate the characteristic phase of wurzite-ZnO (100), (002) and (101) positioned at 2θ = 31.8°, 34.5° and 36.2°, respectively. At certain treatment times, the peak intensities of characteristic XRD peaks and crystallinity of GFZO nanostructures are stronger.

The samples with UV-Ozone treatment time of 18 and 20 min illustrate strong diffraction (002) peak, which indicates high crystalline growth of GFZO nanorods and a stable phase in the ZnO seeding layer films. The strong diffraction (002) peak after UV/Ozone treatment at 18 and 20 min could originate from the obliteration of surface organic contaminants and increase Zn-OH bonding on the surface of ZnO seeding layer. As shown in Fig. 3, the FE-SEM images reveal the GFZO nanostructures grown on ZnO seed layers modified by UV-Ozone treatment at 2, 10, 18and 20 min.

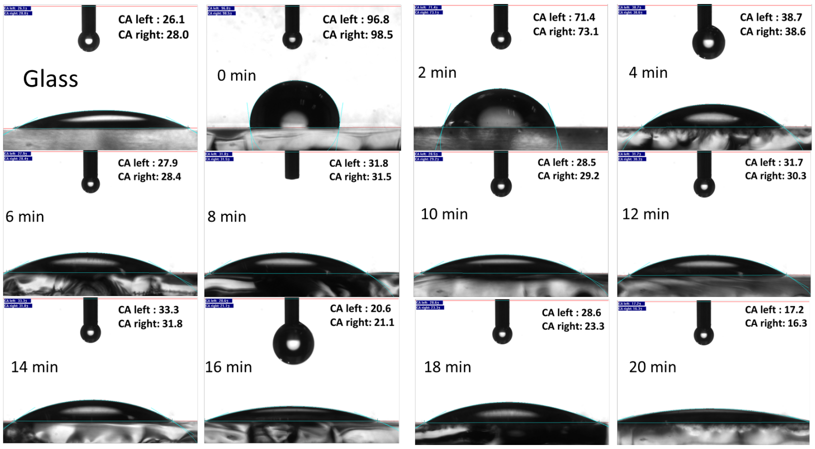

Fig. 1. Contact angles between water droplets on glass and ZnO seeding layers with various UV-Ozone exposure times.

In the case of UV-Ozone treatment at 2, 10 and 18 min, lower density and non-uniform of GFZO nanostructures growth on the ZnO seed layer were observed. The nucleation site density of the wettability on the ZnO seeding layer was insufficient to growth of GFZO nanostructures because of a lower bonding energy for the ZnO seed molecules. After treatment time was increased to 20 min, it is clear that uniform and the highest density growth of GFZO nanostructures is observed due to the increasing wettability number, Zn-OH group and higher bonding energy of the ZnO active nucleation sites during the chemical reaction with the seed layers.

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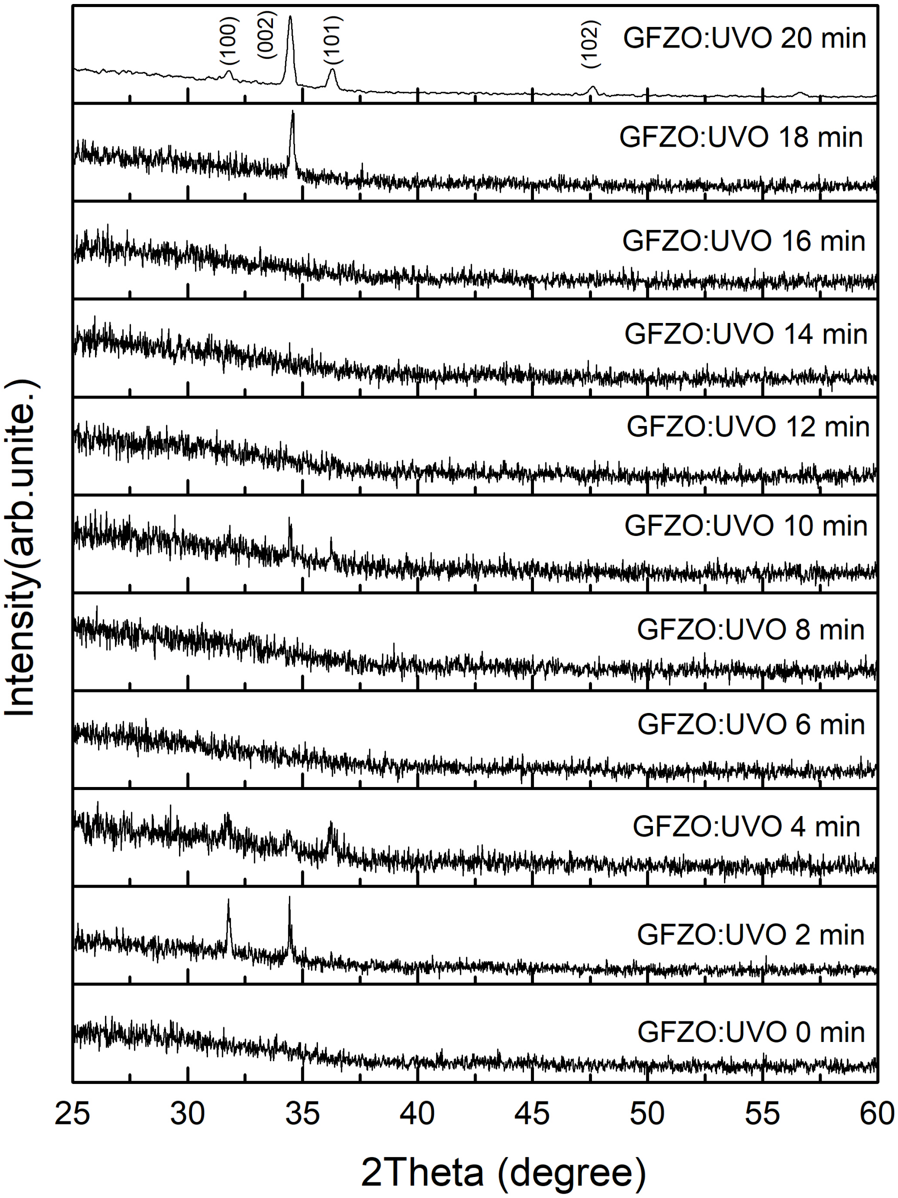

Fig. 2. X-ray diffraction patterns of GFZO nanostructures grown on ZnO seeding layers at various UV-Ozone treatments on seeding layer at 0-20 min.

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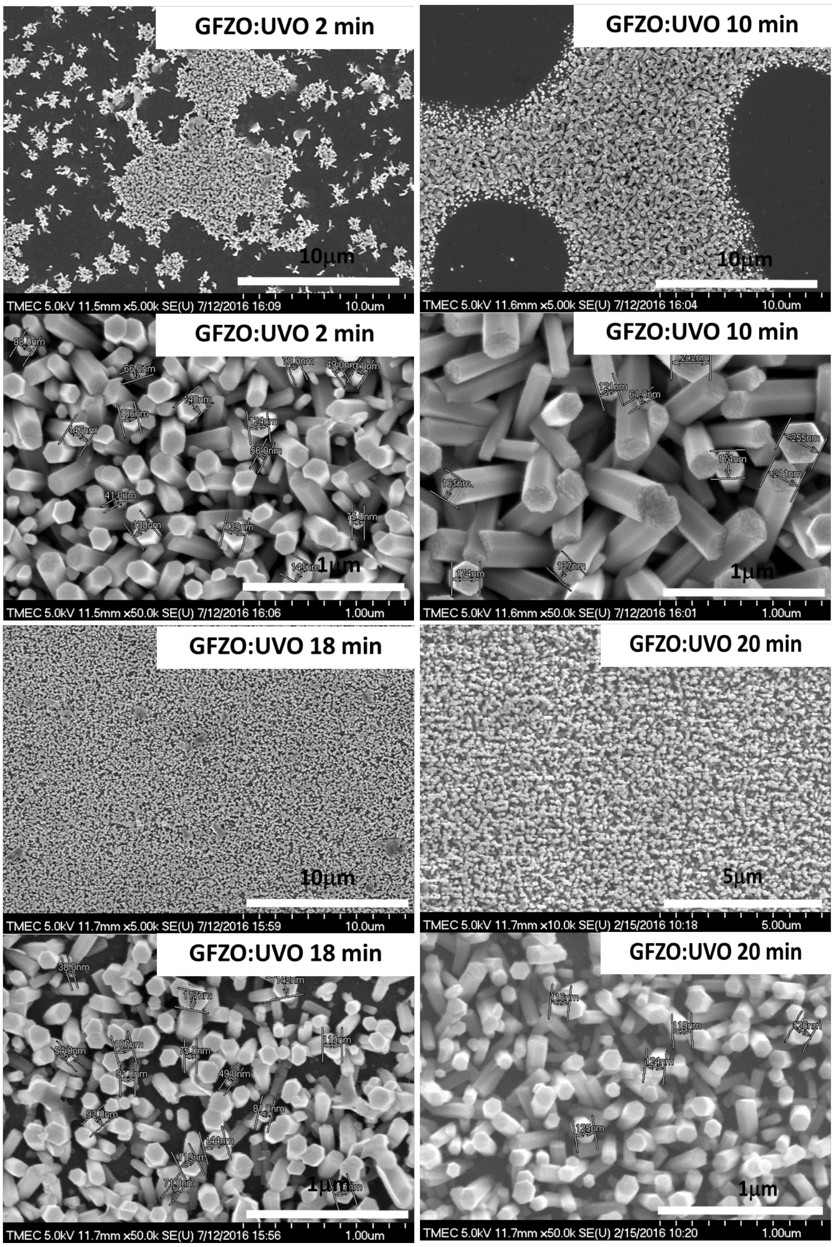

Fig. 3. FE-SEM micrographs of GFZO nanorods grown on ZnO seeding layers after UV-Ozone treatment on seeding layer at 2, 10, 18 and 20 min.

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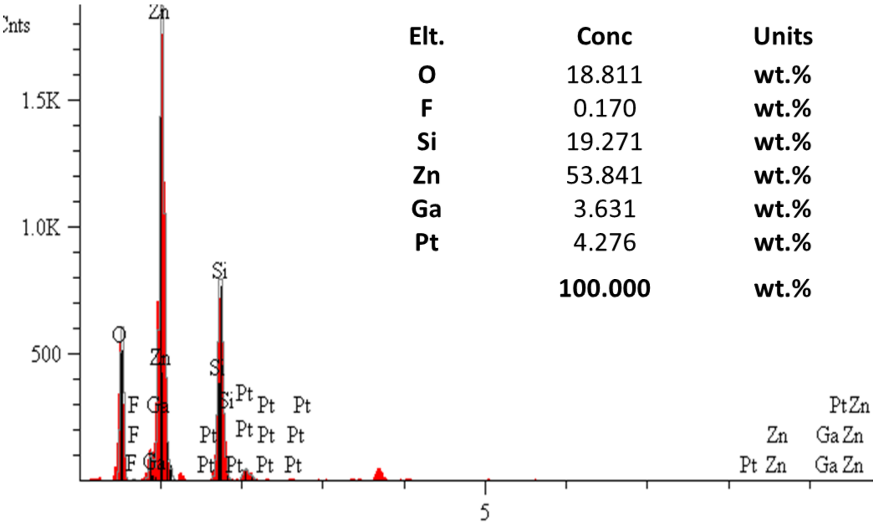

Elt.	Conc	Units
O	18.811	wt.%
F	0.170	wt.%
Si	19.271	wt.%
Zn	53.841	wt.%
Ga	3.631	wt.%
Pt	4.276	wt.%
	100.000	wt.%

Fig. 4. EDS spectrum of Ga-F co-doped ZnO nanostructures grown on ZnO seeding layers.

The incorporation of Ga, F, Zn and O is confirmed by the EDS spectrum of Ga-F co-doped ZnO nanostructures are shown in Fig. 4. The contents of the elements shows in the figure, detected by EDS. The elemental content of the marked area is as follows: Zn = 53.841 wt.%, O = 18.811 wt.%, Ga = 3.631 wt.% and F = 0.170 wt.%. The EDS spectrum shows the well-defined peaks for Zn, O, Ga and F clearly indicate that the Ga-F co-doped ZnO nanostructures are made of Zn, Ga, F and O.

4. Conclusion

The seed layer was successfully prepared by sol-gel dip-coating method. The good surface wettability of ZnO seeding layer using UV-Ozone treatment times at 20 min, which the complete high hydrophilic. Overall results indicated that high hydrophilicity feature on modified ZnO seeding layer especially improvements to strong Zn-OH bonding on the surface from and cleaning surface morphologies which produces a uniform, highest density and high crystallinity growth of GFZO nanostructures confirm by Contact angles, XRD and FE-SEM, respectively.

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