Synthesis of Ga-Doped ZnO Nanoparticles by Solvothermal Method

Huynh Thi Bich Hao[1], Nguyen Thi Thu Hien[1,2], Duong Thanh Tung[1], Nguyen Huu Dung[1], Trinh Xuan Anh[1], Nguyen Duy Cuong[1*]

[1]Hanoi University of Science and Technology – No. 1, Dai Co Viet Str., Hai Ba Trung, Ha Noi, Viet Nam.

[2]Electric Power University, No.235, Hoang Quoc Viet, Hanoi.

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Abstract

In this paper, Ga-doped ZnO nanoparticles (GZO NPs) are synthesized by the solvothermal method from different precursors and with different Ga doping concentrations (0%, 1%, 3%, 5%, 7% and 9%) at the same temperature of 250 °C in the oleylamine solvent. The structural, morphological and optical characteristics were studied by X-ray diffraction, field-emission scanning electron microscope and UV-Vis absorption spectra. Particle size and morphology are strongly influenced by changes in precursor Zn and Ga. The concentration of doping Ga also affects the morphology, structure and optical properties of GZO NPs. When Ga doping concentration increased from 0 to 9%, the nanoparticle size changed in the range of 19-36 nm. GZO NPs have relatively high transmittance. Among the samples with different doping concentrations, the nanoparticles with 5% Ga doping showed the highest transmittance, ~ 85% at the wavelength of 550 nm. This suggests that these nanoparticles are promising to make nanocomposite films applied in transparent conductive electrodes.

Keywords: GZO nanoparticles, solvothermal, particle size, optical properties.

1. Introduction

In recent years, transparent conductive oxides (TCO) have been extensively studied due to their advantages such as low resistivity and high transparency in visible light [1, 2]. Some TCOs have been widely used in applications such as smart windows, solar cells, transparent electrodes in liquid crystal displays (LCDs), OLED organic light-emitting diodes, and etc) [3, 4].

Zinc oxide (ZnO) is an *n*-type semiconductor with a direct bandgap width of 3.37 eV and large exciton binding energy (60 meV) [5, 6]. In addition to its special applications in electronics, catalysts, and sensors, ZnO has the potential in application of transparent conductive oxide (TCO) due to its high conductivity and optical transmission in the visible light region [7], especially when it is doped with IIIA elements such as B, Al, In, and Ga. Among these elements, Ga is the most effective doped element because the ion radius and covalent of Ga are 0.62 Å and 1.26 Å, respectively, which is closer to Zn (0.74 Å and 1.31 Å) in comparison with aluminum (0.5, 1.26 Å) or indium (0.81, 1.44 Å) [8]. In addition, Ga-O covalent bond length (1.92 Å) is similar to Zn-O (1.97 Å) [9, 10]. Therefore, Ga^{3+} can be substituted for Zn^{2+} in a broader range and doping concentration is also higher than that of other metal conductors in the IIIA group with less lattice distortion [11].

In this paper, Ga-doped zinc oxide (GZO) nanoparticles are synthesized by the solvothermal method. To apply as transparent conductive electrode (TCE) films, GZO nanoparticles should be small (less than 30 nm) and the particle size is uniform. To analyze the effect of precursors on morphology and size, we synthesized GZO particles from two different precursor groups at a temperature of 250 °C for an hour with a gallium doping concentration of 5%. Besides, we have also focused on the study of the Ga content affecting the particle size, phase structure, and optical property of the nanoparticles.

2. Experimental

2.1. Material synthesis

The precursors of zinc and gallium used in this research include of (1) zinc acetate dihydrate (purity of 98%, Sigma-Aldrich) and gallium nitrate, 8 hydrate (purity of 99%, Wako-Japan), and (2) zinc acetylacetonate (purity of > 96%, Tokyo Chemical), gallium acetylacetonate (purity of 99.99%, Sigma-Aldrich). Oleylamine (purity of 80-90%, Acros Organics) is used as a solvent.

GZO nanoparticles are synthesized by the solvothermal method with precursor ratios (Ga/(Zn+Ga)) ranging from 0 to 9%. The precursors

* Corresponding author: (+84) 349805375
Email: cuong.nguyenduy@hust.edu.vn

of Zn and Ga were dissolved in 20 ml oleylamine in a three-necked flask in the N_2 gas environment. The mixture was stirred at 60 °C until it dissolves and forms a homogeneous and transparent solution (about 15 minutes), then continued to raise the temperature to 250 °C, and kept at this constant temperature for 1 hour. After finishing the reaction, the solution was cooled slowly to room temperature (about < 40 °C). To separate the nanoparticles, the solution was mixed with a mixture of 4 ml *n*-hexane and 16 ml isopropanol, and then centrifuged at 5500 rpm for 10 min. This washing step was repeated 3 times to make sure that the solvent and unreacted precursors were removed. Finally, the nanoparticles were dried under nitrogen gas flow, and then were dispersed in isopropanol to form stable ink.

The prepared GZO ink is used to fabricate GZO films by doctor-blade printing method (see Figure 1), each sample was printed 2 times on slide glass substrates (Germany).

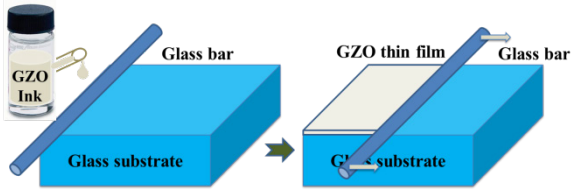

Fig. 1. Schemic of doctor-blade printing method.

2.2. Analyzing methods

The morphology and size of GZO nanoparticles were observed by field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7600F, USA) at BKEMMA Lab, Hanoi University of Science and Technology. The phase structure, preferred orientations and crystallization of nanoparticles were measured by X-ray diffraction (XRD, Siemen D-5005) with the radiation of Cu-K_λ (λ = 1,54056 Å). Transmittance spectra of nanoparticles were recorded by UV-Vis spectrophotometer (Cary 5000 UV-Vis-NIR).

3. Results and discussion

Figure 2 shows the FE-SEM image of these samples. The size of the particles in each sample is quite uniform. However, the particle size of these two samples is very different. The sample synthesized from the precursors $Zn(act)_2$ and $Ga(NO_3)_3$ shows a big particle size, ~55 nm. Whereas nanoparticles fabricated from $Zn(acac)_2$ and $Ga(acac)_3$ depicts small size, ~19 nm. The size of nanoparticles strongly affects the ability to disperse in organic solvents. Normally, large particles are difficult to disperse because they are easy to sink. The dispersion capacity of small nanoparticle is usually better than big size. For this reason, we chose $Zn(acac)_2$ and $Ga(acac)_3$ as precursors of Zn and Ga, respectively, for further studies.

Figure 3 is FE-SEM image of GZO nanoparticles synthesized from various Ga doping concentrations of 0%, 1%, 3%, 5%, and 9% at 250 °C for an hour under N_2 inert gas ambiance. The precursors for Zn and Ga are $Zn(acac)_2$ and $Ga(acac)_3$, respectively. GZO particles are fairly uniform in size and shape. The Ga doping concentration strongly affects the particle size.

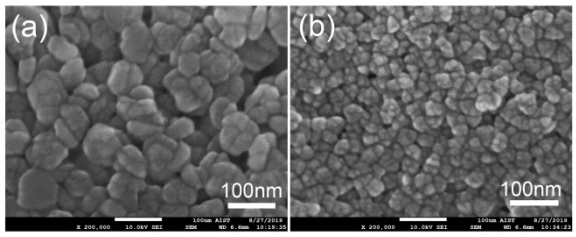

Fig. 2. FE-SEM image of GZO nanoparticles with different precursors of (a) $Zn(act)_2$ and $Ga(NO_3)_3$, and (b) $Zn(acac)_2$ and $Ga(acac)_3$.

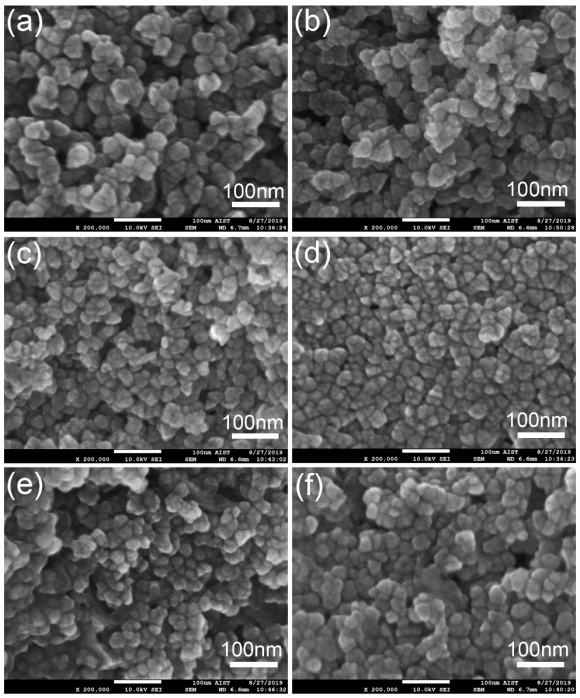

Fig. 3. FE-SEM image of GZO nanoparticles with various Ga doping concentrations of (a) 0%, (b) 1%, (c) 3%, (d) 5%, (e) 7% and (g) 9%.

When the Ga doping concentration increases from 0 to 5%, the size of nanoparticles decreases sharply. Namely, diameter of nanoparticles with Ga doping concentrations of 0%, 1%, 3%, 5%, 7%, and 9% which are calculated from FE-SEM images, are ~ 36, 32, 25, 19, 22, and 31 nm, respectively. These results

were estimated and averaged from 100 GZO nanoparticles based on FE-SEM images with a magnification of 200,000 at a selected area. It is easy to see that the size of GZO grain has a marked change as the concentration of doping increases; namely, the size decreases. At the concentration of 7-9%, the particle size increases again. This is similar to the AZO nanoparticles results reported by Haifeng Zhou *et al* [12] and Ag-doped ZnO [13]. The obtained GZO nanoparticles have a more uniform particle size, and are smaller than that are synthesized by another methods as wet chemical [14].

Figure 4(a) is the XRD pattern of GZO NPs synthesized at different Ga doping concentrations. The diffraction peaks are observed at the positions of 31.86°, 34.50°, 36.32°, 47.66°, 56.70°, 63.06°, and 68.08°, and indexed as preferred orientations of (100), (002), (101), (102), (110), (103), and (112) of ZnO phase with wurtzite structure (JCPDS, No. 36-1451). The second phases such as $Zn_{1-x}Ga_xO_4$ and Ga_2O_3 is not observed in all samples. The peaks are quite strong and sharp, indicating high crystallinity. In addition, to observe carefully the diffraction peaks, the intensity of diffraction peaks decreases gradually when the concentration of doping increases in the range of 0-7%, and it increases at a doping concentration of 9%. This is quite consistent with the variation of particle size as shown FE-SEM images. In the case of the 9% Ga sample, we guess that because the concentration of Ga precursor is too high, it may be preferable to form secondary phases such as Ga_2O_3 instead of replacing Zn^{2+} sites. However, the content of the secondary phase in the sample was very small, so XRD could not detect, so the peaks of these phases did not appear.

The average crystal size of all samples can be calculated from full width half maximum (FWHM) and the angle position of the peak (101) by the Scherrer's formula [15]. GZO NPs have average crystal size at different concentrations: 0%, 1%, 3%, 5%, 7% and 9% is 17.6, 17.1, 16.6, 13.7, 14.1, and 16.5 nm, respectively. The altered crystal size of the GZO (possibly increasing or decreasing) is thought to be due to the ZnO crystal lattice being modified by the concentration of Ga doping [15, 16].

Table 1. Angle of (101) diffraction peak

Sample	2θ (degree)
0%	36.289
1%	36.308
3%	36.316
5%	36.320
7%	36.341
9%	36.327

On the other hand, this size is much smaller than particle size in FE-SEM images. Similar results and trends have been observed by Mridha and Basak [17] for ZnO doped Al nanoparticles. They argued that this is caused by small crystals joining together to form larger particles.

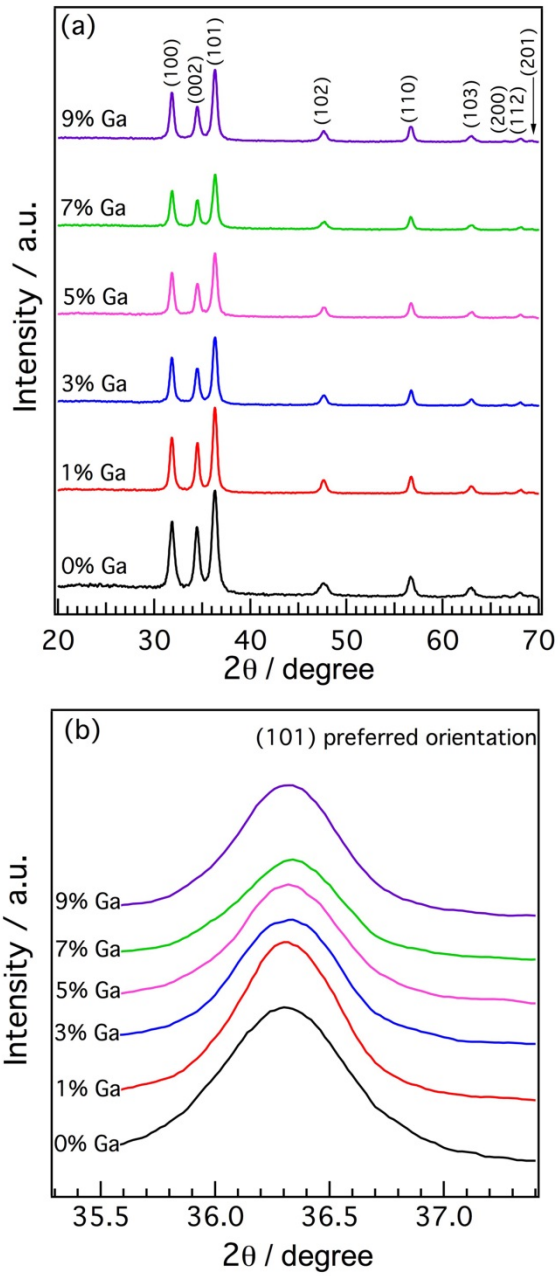

Fig. 4. (a) XRD pattern of GZO nanoparticles with different Ga doping concentrations and (b) the enlarged (101) peak.

Figure 4(b) presents the enlarged crystal (101) orientation. The diffraction peak was shifted gradually towards a larger angle when Ga doping concentration increased (Table 1). However, the shift

of peak is quite small. This can be explained by low doping concentration of Ga in nanoparticles and a small difference in diameter of Zn^{2+} and Ga^{3+}.

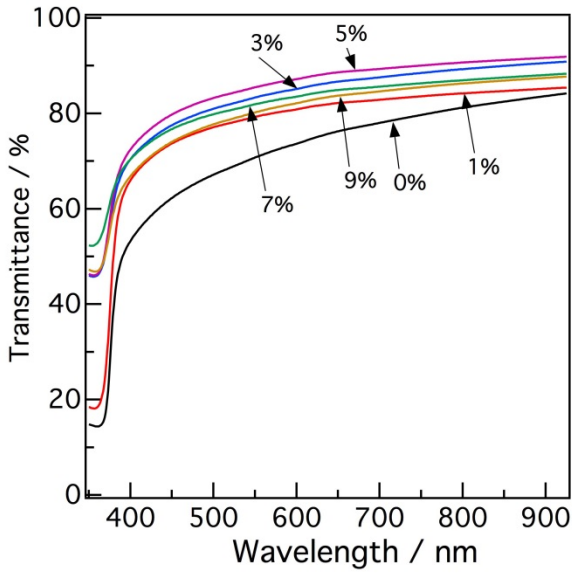

Fig. 5. UV/Vis spectra of GZO nanoparticles with different Ga doping concentration.

To analyzing the optical properties of GZO nanoparticles, GZO nanoparticles were coated on slide glasses for measuring transmittance. The results are shown in Figure 5. In the case of 0% Ga doping concentration, the transmittance at the short wavelengths is rather low. For example, the transmittance at the wavelength of 700 nm is 78%; while it is 67% at the wavelength of 500 nm. However, as the Ga content increases, the transmittance of the GZO nanoparticles in the shorter wavelength is significantly improved. For instance, the transmittance of the GZO nanoparticles with 7% Ga doping at the wavelengths of 500 and 700 nm is 80 and 85% respectively. The improvement of transmittance may be due to the decrease in the size of nanoparticles after doping Ga as shown in the FE-SEM image [18]. J. Ungula and *et al* [19] explained that when larger particles form on the surface of the NP GZO, the scattering of light would occur. This reduces the transmittance of the GZO thin film. Among the synthesized samples, the highest transmittance, ~85% at 550 nm, is observed at the GZO nanoparticles with 5% Ga doping because it has the smallest particle size. Generally, the difference in transmittance at the short and long wavelengths is higher at bigger nanoparticles.

In order to further analyze the relationship between transmittance and particle size of GZO nanoparticle, we calculated the transmittance difference (TD) values at two wavelengths of 500 and 700 nm, in the visible region as follows:

$$TD = (T_2-T_1)/T_1*100\ (\%)$$

In this case: T_1 and T_2 are transmittance at the wavelengths of 500 and 700 nm, respectively. The relationship of *TD* and particle size of GZO is presented in Figure 6. The variation of *TD* and particle size with Ga doping concentration is similar. This shows that the transmittance at a short wavelength is mainly influenced by the size of GZO NPs. This is a common phenomenon for metal oxide nanoparticles reported by several research groups [20, 21].

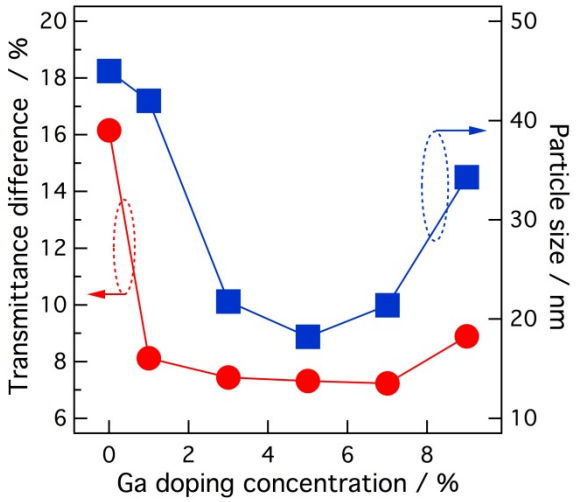

Fig. 6. Particle size and transmittance difference of GZO nanoparticles with different Ga doping concentrations.

4. Conclusions

GZO nanoparticles were successfully synthesized by solvothermal method. Ga doping concentration was strongly affected to the particle size and optical properties of nanoparticles. The size of nanoparticles decreased from 36 to 19 nm when Ga concentration increased from 0 to 5%. The transmittance in the visible region is higher stable at higher Ga concentration. At 550 nm, the highest transmittance was observed at 5% Ga-doped ZnO sample, was ~ 85%. The obtained GZO nanoparticles are promising for applications in the nanocomposite transparent conductive electrode area.

Acknowledgement

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