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Study on fabrication of ZnO nano materials by sol-gen method combining multi-layered spin-coating and heat annealing

Duc-Dung Nguyen[b], , Vu-Loc Pham[b], Quoc-Tuan Nguyen[b], Huu-Cuong Nguyen[a,*]

[a] *Vietnam National University of Forestry National Road 21, Xuan Mai, Chuong My, Hanoi, Vietnam*
[b] *Viet NamInternatinal Training Institute for Materials Science, Hanoi University of Science and Technology, 01 Dai Co Viet, Hanoi, Vietnam*

Abstract

ZnO nano polycrystal materials were fabricated by sol-gel method combining multi-layered spin-coating and heat annealing. Fabricated materials are single phase of hexagonal wurtzite, homogenious with single crystal of spherial shape with 20 – 30 nm size. In this research, ZnO samples were fabricated under different conditions (annealing environment, annealing temperature, number of layers, annealing time...), and then investigated the morphology and crystal structure through XRD, SEM measurements. Optical properties of the samples were investigated through photoluminescen (PL) spectroscopy. The proposed optimal fabrication conditions is annealing in Argon gas at 3500 ^{o}C for 12 h. Samples fabricated in this condition reduce the PL emission regions due to defects.

Keywords: ZnO, sol-gen, SEM, PL, XRD;

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor of group II-VI semiconductors with the nature located at the boundary between covalent and ionic semiconductors. ZnO have a band gap of about 3.4 eV. It has promising electrical and optical catalytic properties. ZnO has been considered a promising material for thin film optoelectronics [1], piezoelectronics [2], transparent electronics [3], spintronics [4], sensors [5] and photoelectricity [6]. ZnO materials fabricated at the nanoscale appear to have many special properties, such as being able to change the form of the luminescen spectrum, or being able to appear ferromagnetic. Therefore, the research and fabrication of nano-sized ZnO materials is of great significance for the practical application.

ZnO materials at nanoscale have been researched and fabricated by many groups by different methods such as: mechanochemical process with precursors of ZnCl2, Na2CO3, NaCl, annealing at 600 ^{o}C for 2h, ZnO particles with size 21-25 nm have hexagonal structure [7]; synthetic method of thermal

* Corresponding author. E-mail: nhcfuv@gmai.com
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solvent, hydrothermal and microwave technique with precursors of Zn(CH3COO)2, Zn(NO3)2, LiOH, KOH, NH4OH, reaction time from 10h-48h at temperature 120–250 °C then ZnO crystals with wurtzite structure of size 100 nm-20μm [8]; sol-gen method with precursors of Zn(CH3COO)2, acid C2H2O4 and ethanol, reaction conditions at 50°C for 60 minutes, gel drying at 80°C for 20h; annealed in air at 650°C for 4h to obtain homogenous ZnO particles with wurtzite structure [9]. In 2018, the research group of Marco Laurenti and colleagues fabricated ZnO materials by vapor phase deposition to create ZnO porous films [10]. Most recently, in 2020, the group of Dominguez et al. fabricated and studied the optical properties of ZnO films by thermal method at 200 ^oC [11].

In this study, we fabricated ZnO materials by sol-gen method combined with annealing in different environments temperatures after the samples being coated with multiple layers on Si substrate. The target is to produce well-crystallized ZnO samples with little defects in lattice of ZnO nano crystals. The effect of fabricated technique on the optical properties of ZnO samples will be studied and discussed. .

2. Experimental

The ZnO materials were prepared by sol-gen method, the precursors were Zinc acetate and DEA. The chemical components with the selected proportions were mixed in the solution with a magnetic stirrer for 5 minutes. Then the solution were heated and magnetically stirred at a temperature of 65-70 oC for 3 hours. After that, the solution sol is cooled down to room temperature. The solution was magnetically stirred for 20 h to stabilize the sol and for thermal hydrolysis. A spin coating machine was used to create a thin films. And then they were put in an annealing furnace at a suitable temperature and annealing environment. The gas environment selected for annealing are O_2, Air and Ar. Annealing temperatures were selected from 350 - 500 ^oC so that the organic matter can be completely destroyed. The annealing time is selected from 1h to 12h. Table 1 summarizes the samples fabricated under different conditions. The number of coating layers (corresponding to the film thickness) is selected as 10, 15, 20, 30.

Table 1. Summary of samples fabricated under different conditions

Samples	Number of Layers	Temperature/Time	Environment
M1	10	500^{o}C/1h	Ar
M2	15	500^{o}C/1h	Ar
M3	20	500^{o}C/1h	Ar
M4	15	500^{o}C/1h	Air
M5	20	500^{o}C/1h	Ar,Air
M6	20	500^{o}C/1h	O_2
M7	10	350^{o}C/12h	Ar
M8	20	350^{o}C/12h	Ar
M9	30	350^{o}C/12h	Ar
M10	10	350^{o}C/12h	O_2

M11	20	350^{o}C/12h	O_2
M12	30	350^{o}C/12h	O_2

The crystal structure and morphology of the materials were studied by X-Ray Diffraction (XRD) on the Bruker D8 Advance system and scanning electron microscopy (SEM) imagines on the FESEM JEOL-JSM7600F system. The optical properties of the samples were studied through photoluminescence (PL) spectroscopy on the HR320 Horiba system.

3. Result and Discussion

It is quite difficult to determine if a material is well crystalline (with few defects in the lattice) or not. With ZnO materials in the form of polycrystalline nanoparticles, through X-ray diffraction measurements, scanning electron microscopy images, we can see a single-phase crystallization pattern, homogeneous morphology. However, when studying the luminescence properties, we usually obtain photoluminescence spectral region cause of the transitions related to the defect levels which come from various types of defects in ZnO lattice (commonly the Oxygen vacancy). In this paper, photoluminescence spectrum is first used as an indicator, an indirect determination to consider whether ZnO nano-polycrystalline samples have more or less defects according to the defect-level emission spectra. The effects of annealing environment, annealing temperature and annealing time, were investigated in detail.

a) Influence of annealing environment

Oxygen, Air and Argon are 3 different annealing environments used to anneal samples for creating of ZnO crystals. In Figure 1, after the blue emission region is normalized, only the PL spectrum of the sample annealed in Argon has a clear emission peak at 380 nm corresponding band-to-band transition. The emission region from 450 nm to 650 nm comes from transitions related to the defect levels. It seems that the crystallization of ZnO becomes better or the defects are reduced in Argon annealing. This leads to a conclusion that annealing in Argon is better than in Oxygen and Air environments. Usually, the sample annealed in an Oxygen or Air atmosphere was thought to reduce the defects of the oxygen vacancy. However, the results shown in Figure 1 contradict the initial predictions. Perhaps, in the presence of Oxygen, organic compounds will be burned or oxidized very strongly, leading to a negative influence on the crystallization of ZnO. Therefore, further fabricated samples should be annealed in an inert Argon atmosphere.

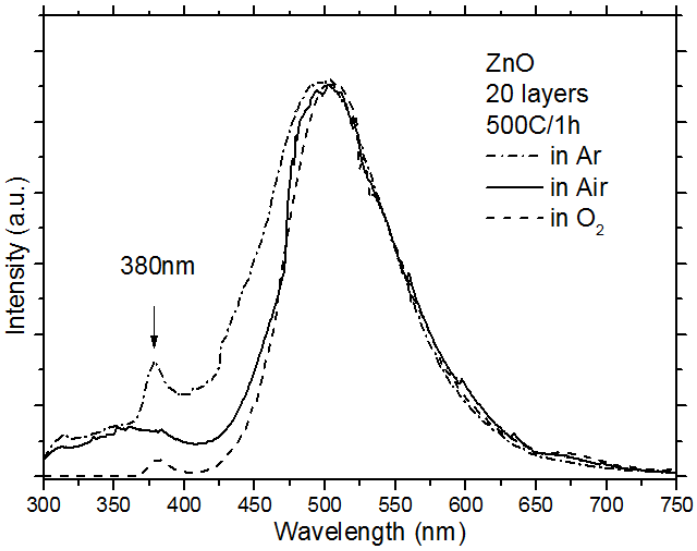

Figure 1. Photoluminescen spectra of 20-layer ZnO thin films, annealed in different environment.

b) Effect of annealing time and temperature

The blue emission peak (500 nm) in the samples with different number of ZnO layers and different annealing environments is still higher than the UV emission peak (380 nm) as shown in Figure 1. Therefore, we try to switch to the other conditions at a lower temperature at 350 ^{o}C with a longer annealing time (12 hours instead of 1 hour), for stabilizing crystallization. Since annealing process is to remove organic compounds and leaving only the heat-stable ZnO solid, lower temperatures can avoid unexpected thermal stresses and allow ZnO crystals forming more slowly and stably over a longer period of time.

Figure 2 presents the photoluminescence spectra of two ZnO samples coated with 20 layers annealed in Ar gas with two different annealing temperature and time, 500^{o}C/1h and 350^{o}C/12h. It is clear that the sample annealed at 350^{o}C/12h has a much larger band-to-band emission peak (380nm) than the sample annealed at 500 ^{o}C/1h. With the sample annealed at 350^{o}C/1h, the intensity of emission peak due to band-to-band transition (380nm) is also many times larger than the maximum intensity of the defect-levels emission region (around 500nm). The appearance of a small peak at 760 nm for samples annealed at 350oC/12h is also evidence of a good luminescence pattern (corresponding to good crystallization) since it is the second harmonic of the 380 nm peak, which occurs only when the 380nm peak intensity is large enough.

After three parameters (annealing medium, temperature and annealing time) were investigated through PL spectroscopy, an optimal annealing conditions were proposed to be 350^{o}C for 12h in Argon gas.

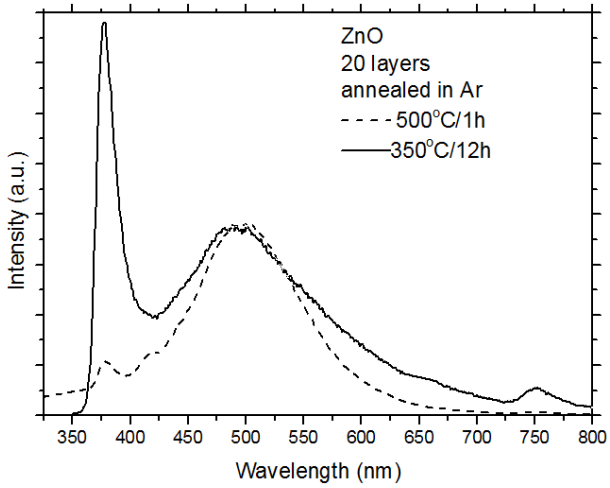

Figure 2. Photoluminesce spectra of different heat treatments for ZnO thin films annealed in Ar environment (with normalized blue emission region).

The samples fabricated under the above conditions were directly studied for structural morphology by X-ray diffraction and scanning electron microscopy. Figure 3 shows the XRD pattern of the 10-layer ZnO thin film. The analysis results indicate that there are only diffraction peaks of the ZnO wurtzite structure, while no diffraction peaks of other crystalline phases are detected. This result proves that the sample is in single phase of hexagonal ZnO wurtzite.

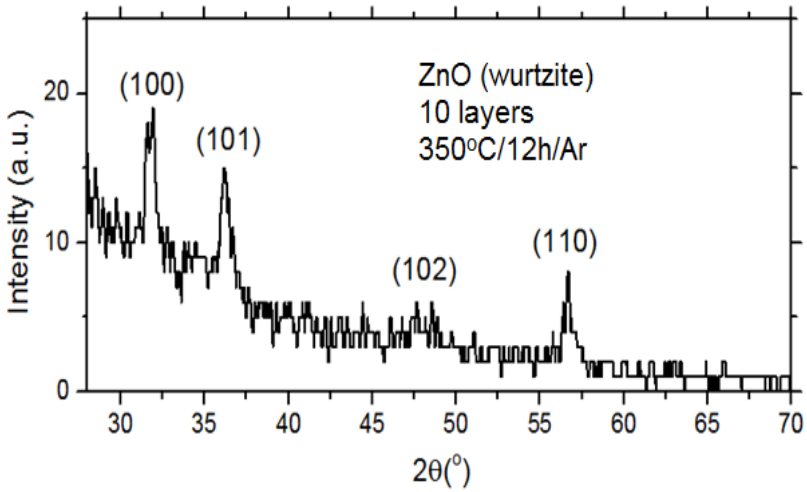

Figure 3. XRD of the 10-layer ZnO thin film.

Figure 4 is the SEM image of the surface morphology of the 10-layer ZnO thin film. Figure 4a shows that the sample surface is uniform over a wide range, where no strange morphology is present, which is consistent with the above XRD analysis. For the higher magnification shown in Figure 4b, the average particle size is only about 20 - 30 nm, the sample is quite homogeneous in terms of size, shape of particles.

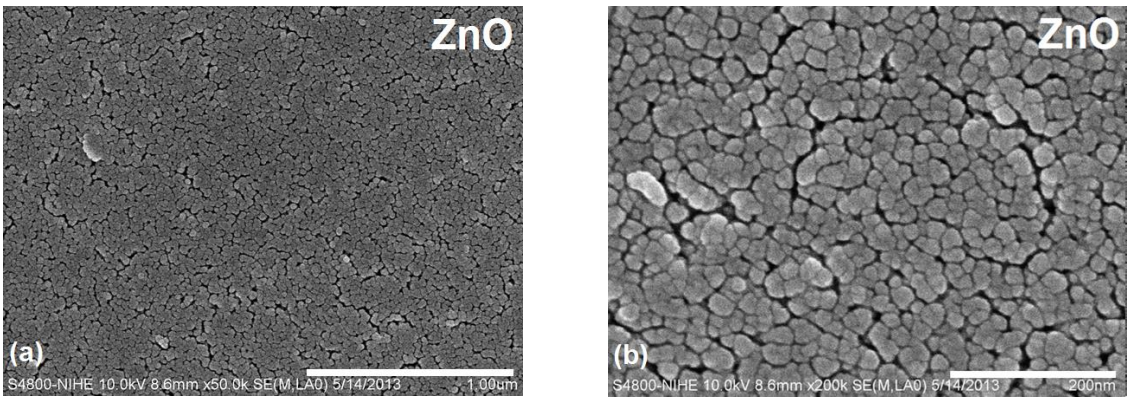

Figure 4. SEM imagines of ZnO thin film in two magnifications of electron microscopy.

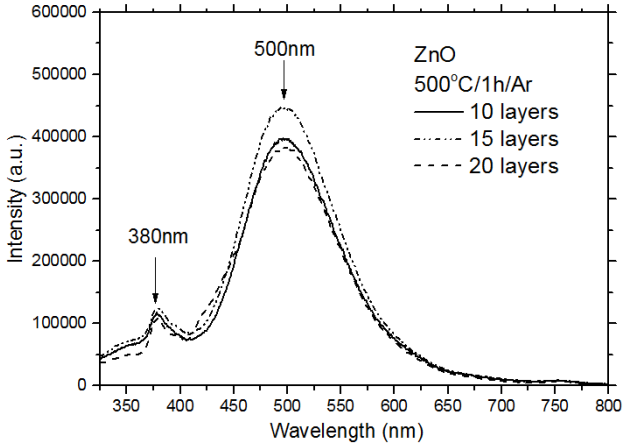

Figure 5. Photoluminesce spectra of the ZnO thin films annealed in Ar environment with the different number of layers.

c) Effect of number of layers

The ZnO thin film samples were made by gel-sol method and then annealed at 500oC/1h in Argon with different number of ZnO layers. First, the samples were investigated by PL spectra, excited by radiation with a wavelength of 296 nm. Figure 5 shows the PL spectrum of ZnO thin films with different number of layers (10 layers, 20 layers and 30 layers). Overall, the three spectra are not significantly different, having the same shape and luminescence intensity. This means that the number of layers does not have much influence on the PL spectrum as well as the structure, morphology and crystallization quality.

4. Conclusions

In this study, we have fabricated ZnO nano polycrystal materials by sol-gel method combining multi-layered spin-coating and heat annealing. The optimal fabrication parameters after research are as follows: Argon atmosphere, annealing temperature of 3500C and annealing time of 12h. The fabricated samples is a single phase hexagonal ZnO wurtzite, homogeneous with spherical single crystal particles with a diameter of 20 - 30 nm. The number of coating layers corresponding to the film thickness did not affect the photoluminescence properties of the samples. With the above fabrication conditions, the sample photoluminescence spectrum have a very large emission peak intensity due to the band-to-band transition at the wavelength of 380 nm, the emission region from the transitions related to the defects levels is reduced significantly. This shows that the number of defects in the lattice of the ZnO samples

is greatly reduced. The results has important implications in controlling and changing the photoluminescence spectrum of ZnO through adjusting parameters (environment, time and temperature of annealing) in the fabrication technology.

Declaration of Competing Interest

The authors declare no competing interests.

Author contributions

Conceptualization: Duc-Dung Nguyen and Huu-Cuong Nguyen; methodology: Vu-Loc Pham and Quoc-Tuan Ta; fabrication: Huu-Cuong Nguyen and Quoc-Tuan Ta; formal analysis: Huu-Cuong Nguyen; investigation: Duc-Dung Nguyen and Huu-Cuong Nguyen; writing original draft: Duc-Dung Nguyen and Huu-Cuong Nguyen. All authors have read and agreed to the published version of the manuscript.

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