Optical properties of ZnO films with nanorod structures

Tianqi Wang, *Ying Wang**, *Jiaxin Li*, *Zhenguo Liao*
School of Science, University of Science and Technology Liaoning, Anshan 114051, China

Abstract: In this paper, ZnO seed layer was prepared on glass substrate by sol-gel method, and ZnO nanorods were grown on the seed layer by hydrothermal method. ZnO films with nanorod structures were obtained. By changing the concentration of hydrothermal growth, different ZnO films with nanorod structures were obtained, and the structure, morphology, transmittance and light trapping properties of the films were characterized. The optical properties of ZnO films with nanorod structures under different growth conditions were studied in order to improve the light trapping properties of ZnO films while ensuring high transmittance of the films.

Key words: ZnO thin films; Nanorod; Transmittance; Light trapping

I. Introduction

In recent years, ZnO-based films have gained attention and research in the field of optoelectronics, which are widely used in flat panel displays, solar cells, light-emitting diodes and other optoelectronic devices. This is because ZnO-based films have not only excellent optoelectronic properties, but also abundant source materials, low cost and high stability in special environments. In terms of optical properties, ZnO films have high transmittance of about 90% in visible light region and high reflectivity in the infrared region. Therefore, ZnO films can be used as infrared reflective films. In terms of electrical properties, doped ZnO films have low resistivity, which can reach the order of 10^{-4} Ω·cm. Therefore, doped ZnO films can be used as transparent electrodes in optoelectronic devices. In addition, in order to improve the utilization of light, the effective light trapping effects can be achieved when the microstructures are obtained in the ZnO films. The textured structure is a kind of surface morphology feature, which is the specific morphology of the light trapping structures. ZnO films with textured structures, due to the high surface roughness, can increase the optical path of the incident light, and then improve the light trapping abilities of the films. And they have been widely used in many optoelectronic devices, showing a very broad prospect for development. Obtaining textured films with high light trapping abilities at low cost is one of the key technologies to further improve the performance of optoelectronic devices.

In this paper, ZnO seed layer was prepared on glass substrate by sol-gel method, and ZnO nanorods were grown on the seed layer by hydrothermal method. Nanorod structured ZnO thin films with excellent optical properties were obtained. The structure, morphology, transmittance and light trapping properties of ZnO films obtained under different hydrothermal growth concentrations were characterized, and the optical properties of nanorod structured ZnO films with different morphologies were compared.

II. Experimental

1. Preparation

According to the concentration of ZnO (0.03 mol/L), the mass of the reactant zinc dihydrate acetate ($Zn(CH_3COO)_2·2H_2O$) was calculated and weighed accurately using an electronic balance. $Zn(CH_3COO)_2·2H_2O$ was dissolved in anhydrous ethanol to obtain solutions, and the magnetic stirrer was used to stir the solution fully. Then, the solutions were aged. After ultrasonic cleaning, the glass substrate was dried for use. The prepared solutions were spin coated on the glass substrate, and then dried to obtain ZnO seed layers with uniform surface. spin coating and heating process were repeated to obtain ZnO seed layers with a certain thickness. The glass substrate with ZnO seed layers was placed in a Muffle furnace and annealed for 30 min at 350°C.

Aqueous solutions of $Zn(CH_3COO)_2·2H_2O$ and $C_6H_{12}N_4$ were obtained according to the molar concentration ratio of 1:1, and thoroughly stirred using the magnetic stirrer. The glass substrate with the ZnO seed layers was placed in the Teflon-lined autoclave apparatus with the prepared reaction solutions for growth in the oven at 90°C for 3 h. After the reaction, the samples were rinsed with deionized water and dried. The hydrothermal growth concentration was changed (0.05 mol/L, 0.07 mol/L and 0.01 mol/L). The detailed experimental parameters were shown in Table 1.

Table 1 Experimental parameters

Sample	$Zn(CH_3COO)_2·2H_2O$	$C_6H_{12}N_4$	Heating temperature	Heating time
	(mol/L)	(mol/L)	(°C)	(h)
1	0.05	0.05	90	3
2	0.07	0.07	90	3
3	0.1	0.1	90	3

2. Characterization

The prepared films were characterized. The surface morphology of the samples was observed by field-emission scanning electron microscope (SIGMA HD). The optical properties and light trapping properties of the films were measured by UV-Vis-NIR spectrophotometer with an integrating sphere. The structural properties of ZnO films were characterized by XRD.

III. Results and discussion

1. Structural properties

Fig. 1 shows the XRD pattern of ZnO thin films prepared at the reaction concentration of 0.05 mol/L. It can be seen that a strong diffraction peak appears at 2θ of 34°. The position of this diffraction peak is compared with the standard XRD card (JCPDS No. 36-1451), which corresponds to the (002) crystal plane of hexagonal wurtzite ZnO. This indicates that the prepared ZnO thin films grow preferentially along the c-axis perpendicular to the substrate, which is also consistent with the following SEM results.

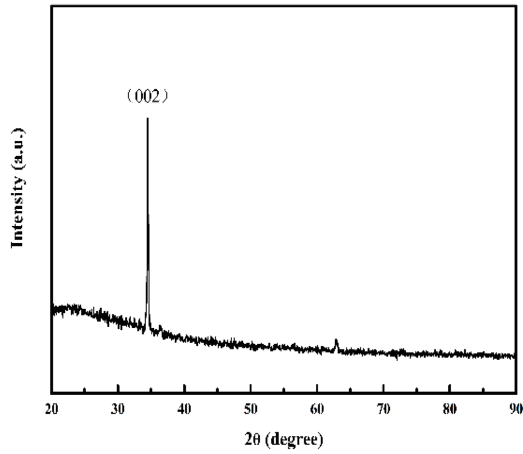
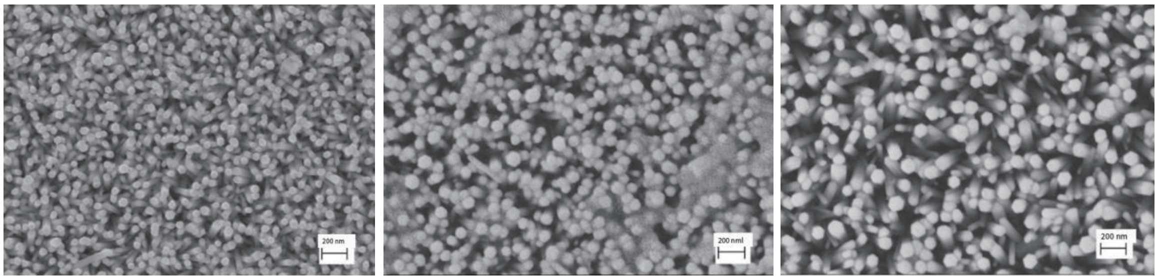


Fig. 1 XRD pattern of ZnO films at the reaction concentration of 0.05 mol/L

2. Surface Morphology

SEM are conducted on ZnO films prepared under different reaction solution concentrations, as shown in Fig. 2. It can be found that the surface morphology of ZnO films changes with the concentration of the reaction solution. From Fig. 2 (a), (b) and (c), it can be seen that the nanorod structures are obvious. The top morphology of the nanorods tends to be hexagonal, and the ZnO nanorods grow preferentially perpendicular to the substrate. From Fig. 2 (c), it can be seen that when the concentration of reaction solution reaches 0.1 mol/L, the growth of some ZnO nanorods is inclined to a certain angle with the substrate. The presence of gaps among the nanorods can be observed. With the increase of the concentration of the reaction solution, the diameter of the nanorods increases gradually. The top shape, vertical orientation and diameter of ZnO nanorod structures affect the light trapping properties of the films. The relationship between the nanorod structures morphology and the light trapping ability is given in the following haze spectra results and analysis.



(a) (b) (c)

Fig. 2 SEM images of ZnO films at different reaction solution concentrations :(a) 0.05 mol/L, (b) 0.07 mol/L, (c) 0.1 mol/L

3. Optical properties

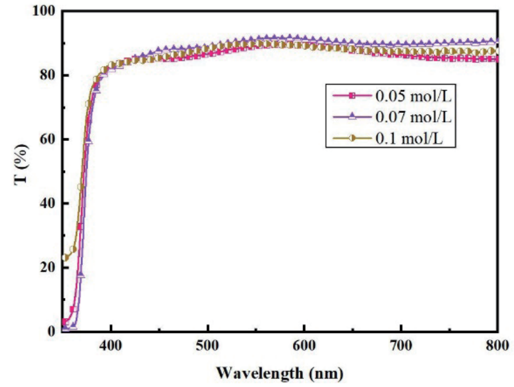


Fig. 3 Transmittance spectra of ZnO films prepared under different reaction solution concentrations.

Textured ZnO films must have high visible light transmittance. Fig. 3 shows the transmittance spectra of ZnO films prepared under different reaction solution concentrations. It can be seen from the Fig. 3 that all the ZnO films prepared under different reaction solution concentrations have a steep absorption edge at a wavelength of about 370 nm. And the steep absorption edge has a redshift as the concentration increases. In the range of visible light band (400 nm-800 nm), the average visible light transmittance of the films prepared under different reaction solution concentrations reaches 80%, which indicates that all ZnO films have good visible light transmittance, meeting the application needs in optoelectronic devices.

4. Light trapping properties

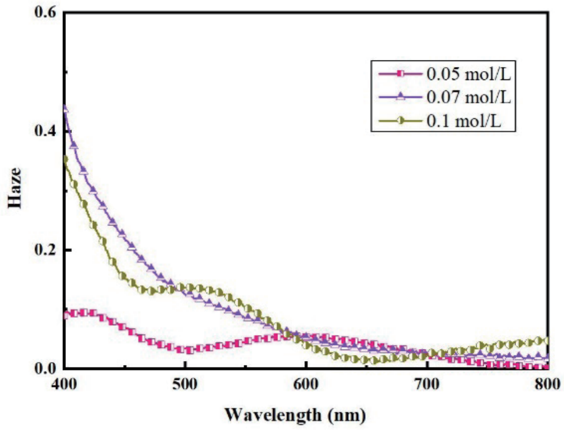


Fig. 4 Haze spectra of ZnO films at different reaction solution concentrations.

Fig. 4 shows the haze spectra of ZnO films prepared under different reaction solution concentrations. The haze value shows the light trapping abilities of the films. The larger the haze value, the stronger the light trapping abilities of the films. As can be seen from Fig. 4, the haze value of ZnO films prepared under different reaction solution concentrations is greater than 0 in the visible light range, indicating that all the prepared films have light trapping abilities. With the increase of the concentration of the reaction solution, the haze value of the films is increased gradually, indicating that the light trapping abilities gradually become stronger. Combined with the SEM results, it can be seen that the light trapping abilities of the films are closely related to the microstructure of the film surface. When the concentration is 0.1 mol/L, the nanorod structures are evenly distributed and relatively sparse. And the diameter is large, so the films have good light scattering effects and light trapping abilities.

IV. Conclusions

In this paper, ZnO seed layer was prepared on glass substrate by sol-gel method, and ZnO thin films with nanorod structures were grown by hydrothermal method on the seed layer by changing the concentration of reaction solution. Through a series of characterization, the XRD pattern showed a strong (002) crystal plane diffraction peak, indicating that ZnO films had good crystal quality and grew along the c-axis. With the increase of reaction concentration, the surface morphology of ZnO films was changed obviously, and the diameter of ZnO nanorods increased gradually. The total transmittance of ZnO films in the visible light region exceeded 80%. When the reaction concentration was 0.1 mol/L, the haze value of ZnO films was higher, which indicated that ZnO films had good light trapping properties.

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* Corresponding author: Ying Wang

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