Preparation and properties of ZnO-based nanostructured films with light trapping effects

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Abstract: In this paper, ZnO-based nanostructured films were prepared by hydrothermal method on ZnO seed layers obtained by sol-gel method and AZO transparent conductive glass. XRD, SEM, sheet resistance test, transmittance and haze spectra were used to characterize the structure, morphology, optoelectronic properties and light trapping abilities of the films. The effects of seed layer concentration and hydrothermal growth temperature on the characteristics of ZnO-based nanostructured films were studied, and the prepared films had light trapping effects and high total transmittance in the visible light region.

Key words: ZnO-based thin films; Nanostructure; Optoelectronic properties; Light trapping effect

1. Introduction

Transparent conductive oxide films have been widely used in solar cells because of their excellent optoelectronic properties. The introduction of the light trapping structures in the films as the front electrodes of the solar cell can increase the path of the incident light in the absorption layer and effectively improve the conversion efficiency of the cells.

ZnO has the advantages of wide band gap and high transmittance in the visible region. Doping Al, Ga and other elements can improve the electrical conductivity of ZnO. ZnO-based nanostructured films with light trapping effects can be obtained by various methods. And the sol-gel method, hydrothermal method and other wet chemical methods have the advantages of simple technology, low cost and low growth temperature.

In this paper, ZnO-based nanostructured films were prepared by hydrothermal method on ZnO seed layers obtained by sol-gel method and AZO transparent conductive glass. The morphology, structure, optoelectronic properties and light trapping abilities of ZnO-based nanostructured films prepared at different seed layer concentrations and hydrothermal growth temperatures were studied.

2. Experimental

2.1 Preparation of ZnO nanostructured films

ZnO seed layer solutions with concentrations of 0.005 M, 0.015 M, 0.02 M and 0.03 M were prepared by dissolving $Zn(CH_3COO)_2 \cdot 2H_2O$ in ethanol and were aged for 12 h. The seed layer solutions were evenly coated on the glass substrate by spin coating method. And then the samples were placed in the oven at 100°C. The above process was repeated for 8 times. The samples were annealed at 350°C for 30 min. Subsequently, ZnO nanostructured films were grown by hydrothermal method. $Zn(CH_3COO)_2 \cdot 2H_2O$ and $C_6H_{12}N_4$ aqueous solution at equal concentration of 0.03 M were mixed and stirred at room temperature and poured into a Teflon-lined autoclave apparatus containing seed layer samples. After sealing, the samples were grown in an oven at 90°C for 2 h. Finally, the samples were rinsed with deionized water and dried.

2.2 Preparation of AZO nanostructured films

AZO nanostructured films were grown on AZO transparent conductive glass by hydrothermal method. $Zn(CH_3COO)_2 \cdot 2H_2O$ and $C_6H_{12}N_4$ with molar concentrations of 0.1 M were used as precursors, and $Al(NO_3)_3 \cdot 9H_2O$ was added as doping source (Al: 2 mol%). After stirring and dissolving, the solutions were poured into the Teflon-lined autoclave apparatus for hydrothermal growth in the oven at different temperatures (70°C, 80°C, 90°C, 100°C) for 3 h. Finally, the samples were rinsed with deionized water and dried.

2.3 Characterization

The morphology of the films was analyzed by field-emission scanning electron microscopy. The crystal structure of the films was measured by X-ray diffraction (XRD). The transmittance and haze spectra of the samples were measured by UV-Vis-NIR spectrophotometer with an integrating sphere. The sheet resistance of the films was measured by an RTS-8 four-point probe instrument.

3. Results and discussion

3.1 ZnO nanostructured films

Fig. 1 shows the SEM images of ZnO films prepared under different seed layer concentrations. When the seed layer concentration is 0.005 M, the surface of the film shows the rough blocky structures. This may be because the concentration of the seed layer is too low, which affects the nucleation process of ZnO seed. With the increase of the seed layer concentration, hexagonal ZnO nanorod structures in the direction perpendicular to the substrate can be seen obviously. And there are more gaps among the nanorods. When the seed layer concentration is increased to 0.03 M, the nanorod structure become denser. In addition, it can be seen from Fig. 1(b)-(d) that the ZnO nanorods of all samples are uniform in size and smaller in diameter, and the surface of the films is denser.

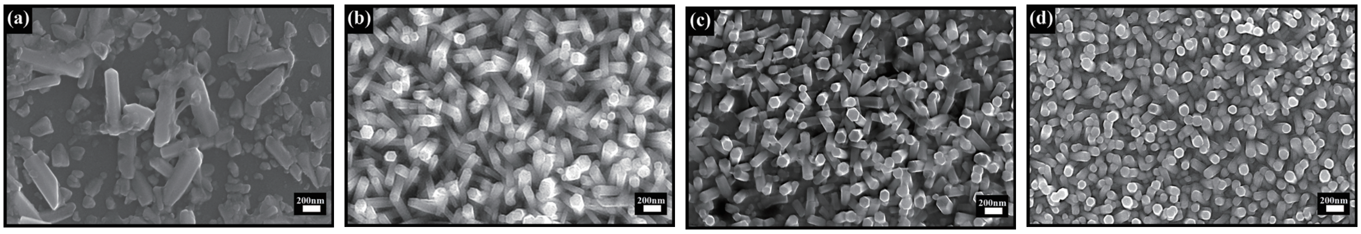
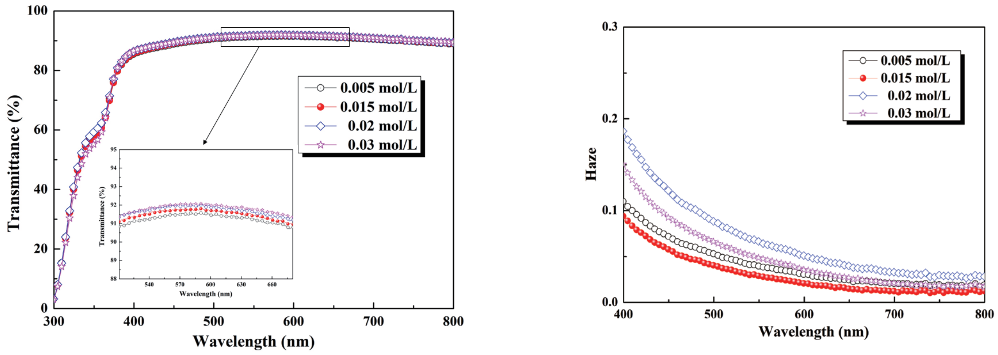


Fig. 1 SEM images of ZnO nanostructured films at different seed layer concentrations:
(a) 0.005 M, (b) 0.015 M, (c) 0.02 M and (d) 0.03 M

Fig. 2(a) shows the total transmittance spectra of all ZnO nanostructured films. The average total transmittance of all ZnO films reaches 90% and increases with the increase of seed layer concentration. At the same time, all the samples have a steep absorption edge in the UV region. Fig. 2(b) shows the haze spectra of ZnO films at different seed layer concentrations. The haze values of the films are all greater than 0 in the visible light region, indicating that the prepared ZnO nanostructured films have light trapping effects. When the concentration of seed layer is 0.02 M, the haze value of the films reaches 0.07 at 550nm. The light trapping ability of ZnO films is closely related to the surface microstructure. The large tilt angle of nanorods leads to more gaps among the nanorods, which will enhance the light scattering and the light trapping abilities.



(a) (b)

Fig. 2 (a) Total transmittance spectra and (b) haze spectra of ZnO nanostructured films at different seed layer concentrations.

3.2 AZO nanostructured films

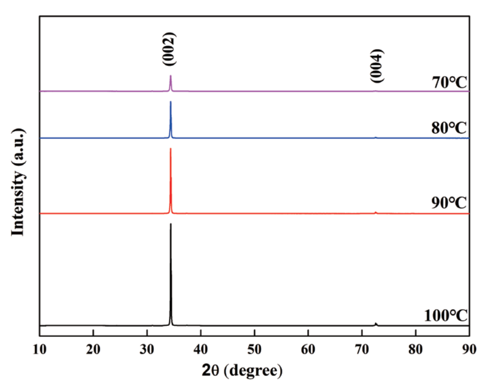


Fig. 3 XRD patterns of AZO films at different hydrothermal temperatures.

Fig. 3 shows the XRD patterns of AZO films under different hydrothermal temperatures. All the films have a strong and weak diffraction peak at 2θ of 34.4° and 72.5°, corresponding to the (002) and (004) crystal plane of hexagonal wurtzite ZnO, respectively. The AZO nanostructures grow preferentially along the c-axis perpendicular to the substrate. The intensity of (002) peak is increased with the increase of hydrothermal temperature, indicating that the crystalline quality of the films is improved with the increase of hydrothermal temperature.

Fig. 4 shows the SEM images of AZO nanostructured films under different hydrothermal temperatures. At 70°C, only a small number of irregular hexagonal AZO nanorod structures can be seen on the surface of the film. This may be due to the relatively slow nucleation and growth rate of AZO nanorods at low temperature. As the growth temperature is increased gradually, the hexagonal AZO nanorods are clearly visible and increased. It can be seen from the above results that with the increase of growth temperature, the morphology of ZnO changes from a network-like structure to a nanorod-like structure. At 100°C, more gaps are observed among the nanorods, as shown in Fig. 4(d).

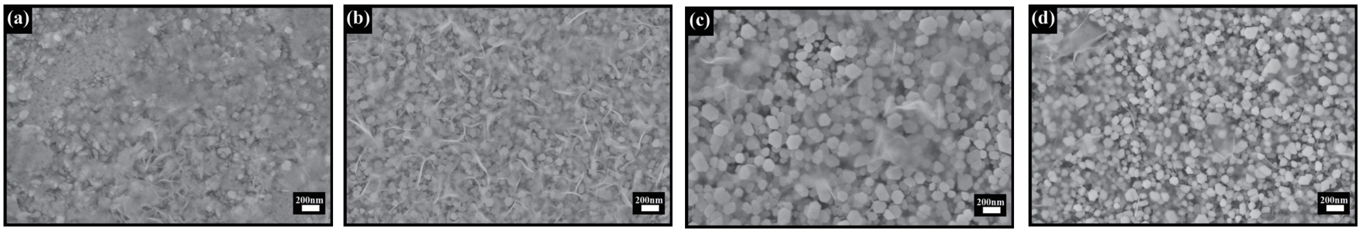
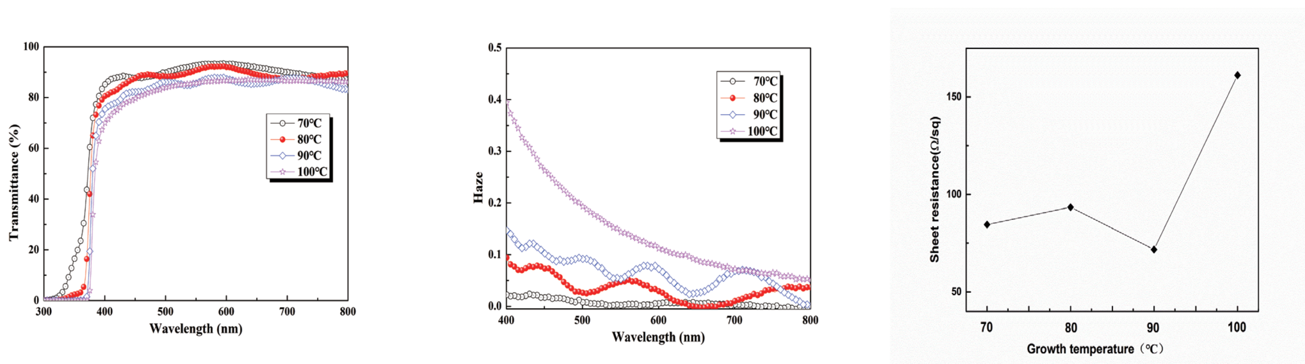


Fig. 4 SEM images of AZO nanostructured films at different hydrothermal temperatures: (a)70℃, (b)80℃, (c)90℃, (d)100℃

Fig. 5(a) shows the total transmittance spectra of all AZO nanostructured films. All films have a high average total transmittance of 80% in visible light region. As the hydrothermal temperature increases, the steep absorption edge is redshifted in the UV region. Fig. 5(b) shows the haze spectra of all AZO nanostructured films. The haze value increases with the increase of hydrothermal temperature. Compared with the network-like AZO films, the nanorod-like AZO films have higher haze value. It can be seen from SEM and haze spectra that the haze value increases with the appearance of a large number of nanorod structures on the surface of the samples. When the hydrothermal growth temperature is 100℃, there are more gaps among the nanorods on the surface of AZO nanostructured films, which is beneficial for improving the light trapping abilities of the films. And the high haze value of 0.14 is obtained at 550 nm. Fig. 5 (c) shows the sheet resistance of AZO nanostructured films at different hydrothermal temperatures. When the hydrothermal temperature rises from 70 ℃ to 90 ℃, the sheet resistance value of the films is about 70-90 Ω/sq, which is relatively low. When the hydrothermal temperature is 100℃, the film has a higher sheet resistance value of about 160 Ω/sq than the other three samples.



(a) **(b)** **(c)**

Fig. 5 (a) Total transmittance spectra, (b) haze spectra and (c) sheet resistance of AZO nanostructured films at different hydrothermal temperatures.

4. Conclusions

In this paper, ZnO-based nanostructured films with light trapping effects were prepared by hydrothermal method on ZnO seed layers obtained by sol-gel method and AZO transparent conductive glass. XRD results showed that the prepared ZnO-based nanostructured films were typical hexagonal wurtzite structures. The average total transmittance of all the samples in the visible light range was more than 80%. The morphology of ZnO nanostructured films varied with the concentration of seed layers. The ZnO nanostructured films prepared at the seed layer concentration of 0.02 M had the highest haze value. With the increase of hydrothermal temperature, the surface morphology of AZO nanostructured films changed from network-like to nanorod-like structures. The AZO films prepared at 100℃ had higher haze value. In addition, AZO nanostructured films also exhibited low sheet resistance.

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