

Preparation of ZnO membrane by chemical bath deposition method via regulated acidity

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Abstract

In this study, the chemical bath deposition (CBD) method was used to deposit a ZnO membrane on an indium tin oxide glass substrate. The deposition reaction working temperature was 90°C and the temperature retaining deposition time was 60 min; NH_4OH was used to control the pH value in the range 10~11, and after deposition, the specimen was thermally annealed in air. Annealing temperatures in the range of 100~500°C were adopted to investigate the thin-film growth behavior and the effect of processing temperature on the ZnO membrane performance during the annealing process. The process parameters related to the preparation of the ZnO membrane by CBD were the pH value, retaining temperature deposition time, working temperature for the deposition reaction, annealing thermal processing, and so on. Scanning electron microscopy (SEM) was used to observe and analyze the surface morphology and microstructure of the membrane cross section, and UV-Vis spectrometry was used to measure the optical transmission of the ZnO membrane in air at different annealing temperatures. We investigated the effects of different pH values on the growth of the ZnO membrane by CBD. The experimental results show that at a pH of 10.7, we can obtain a transparent and electrically conductive ZnO thin film with a thickness of 240 nm, which has very good optical transmission and high electrical mobility at an annealing temperature of 200°C.

Keywords: Chemical bath deposition, ZnO membrane, pH value

1. Introduction

ZnO is a II-VI semiconductor material having a hexagonal wurtzite structure and an energy band gap of about 3.3 eV; it has high transmission in the visible region and very steep transmission in the near-UV region; it has wide applicability in piezoelectric, optoelectronic, pressure-sensitive, and gas-sensitive devices. Various methods have been used to prepare a ZnO membrane, including chemical spray pyrolysis[1], metal-organic chemical vapor deposition[2], RF sputtering[3], sol-gel[4], pulsed laser deposition[5], continuous ionic layer absorption reaction deposition[6], and chemical bath deposition (CBD) [7~9]. The CBD method is a liquid deposition technique for thin films, in which a cleaned substrate is dipped into the deposition reaction solutions. It does not require application of an external electric field or other external energy, and the reaction can be carried out by controlling the chelation and precipitation of the reactants under normal pressure and low temperature (30~90°C). An inorganic thin film can be deposited on a substrate by this method. In order to deposit a ZnO membrane by CBD, Zn^{2+} ions should be released slowly in the form of the chelating compound $Zn(NH3)4^{2+}$. Addition of an appropriate amount of pH adjusting agent (NH_4OH) to the reaction solution can enable precise control of the pH value in the range of 10~12. The process parameters for the preparation of the ZnO membrane by CBD include deposition temperature, deposition time, concentration ratio of the reaction solution, types of chelating compounds and additives, pH values, and so on. In the preparation process of the ZnO thin film using CBD, two competitive growth mechanisms are usually observed to occur: homogeneous deposition in the solution and heterogeneous deposition[10]in the substrate. Heterogeneous deposition includes two possible routes: **(a)** adsorption of ZnO particles on the substrate, which is a cluster-by-cluster mechanism and would lead to a rough and loose surface on the ZnO membrane; and (b) ion-by-ion mechanism, in which the Zn^{2+} chelating compound is adsorbed onto the substrate first, and then, through medium-phase thermal decomposition, an ultrathin ZnO membrane is obtained. Generally speaking, the obtaining of dense and flat ZnO transparent and electrically conductive thin film through route (b) is what we expect. In this study, we evaluate the effect of pH value on the microstructure, thickness, and optical transmission of the ZnO membrane synthesized by the CBD method.

2. Experimental

A Zn ion source, i.e., 0.4-M zinc acetate with NH_4OH, was used as the precursor for the preparation of the ZnO membrane by CBD. Deionized (DI) water was added to the precursor to prepare the reaction solution. After the precursor solution was prepared, it was placed on a digital heater and agitator. Then, NH_4OH was added to the reaction solution and the pH value of the solution was controlled within the range 10~11. Next, a glass substrate (dimensions: 75 mm × 25 mm × 1 mm) was separately immersed in acetone, alcohol, and DI water; each assembly was subjected to ultrasonic vibration for 15 min; then, it was wiped clean and the CBD deposition reaction was carried out. The CBD reaction tank was heated to a temperature of 90°C and the glass substrate was dipped in the reaction solution. Agitation was performed at a fixed speed using a magnetic stone, and the retaining temperature deposition time was 30 min. After this time, the precursor formed the ZnO membrane on glass substrate surface. By increasing the reaction time, the desired thickness of the ZnO nanomembrane could be attained. Next, the glass substrate was removed and rinsed repeatedly with DI water to remove any residual ZnO particles and impurities. Then, the specimen was dried in air at a temperature of 30~60°C. The specimen was then annealed at a temperature of 100~500°C; the time control in the temperature rising section is 25 s, retaining time is 5 min, and the temperature falling time is 30 min. Characteristics of the membrane specimen were measured in air. Then, scanning electron microscopy (SEM) was used to analyze the surface microstructure of ZnO/glass and measure the thickness of the thin film. UV-Vis spectrometry was used to measure the optical transmission of ZnO/glass**.** Figure 1 shows the flowchart of the membrane preparation process by CBD. Table 1 lists the experimental parameters for this preparation at different pH values.

3. Result and Discussion

3.1 Influence of pH value on surface morphology and cross section of ZnO thin film

Figure 2 shows the SEM microstructure of the prepared ZnO thin film at pH values of 10.7 and 11. Here, the reaction working temperature was 90°C and the temperature retaining deposition time was 60 min. Figure 2 shows that the membrane prepared with 9 ml NH4OH at a pH of 10.7 has a more uniform and denser surface morphology; however, the crystal size is smaller, about 70 nm. When the pH value is continuously increased to 11, obvious porosity and a non-homogeneous surface morphology can be seen among crystals on the thin film surface; in this case, the crystal size is larger, about 200 nm, but many pores and defects exist among the crystals. Figure 3 shows the cross-sectional SEM images of the ZnO membrane prepared at different pH values by CBD. this image shows that the growth rate and thickness of the ZnO membrane prepared at a pH of 10.7 and annealing temperature of 200°C are about 4 nm/min and 240 nm, respectively. When the pH value is continuously increased to 11, the deposition rate increases considerably to 7 nm/min, with a thickness of about 430 nm. Under the condition of pH = 11, ZnO crystals will grow very fast, because of which it will not be possible to grow a thin film with a flat surface and without any pores.

3.2 Influence of thermal annealing on surface morphology of ZnO membrane

Figures 4 and 5 show the SEM microstructure and X-ray diffraction (XRD) pattern, respectively, of the ZnO membrane prepared at annealing temperatures of 100, 200, 300, 400, and 500°C; the CBD conditions were a reaction working temperature of 90°C, temperature retaining deposition time of 30 min, and pH of 10.7. Here, it can be seen that a higher annealing temperature is better for obtaining a denser ZnO thin film and reducing pores. In addition, the surface of the ZnO membrane prepared at pH of 11 is worse than that of the membrane prepared at pH of 10.7.

3.3 Measurement of optical transmission of ZnO thin film

Figure 6 shows the optical transmission of the ZnO membrane measured at pH = 10.7 and at annealing temperatures of 100, 200, 300, 400, and 500°C in the spectral range of 300~800 nm. We observe that the ZnO membrane prepared at the annealing temperature of 200°C has the best transmission, and in the visible region (400~700 nm), the transmission change is 80~85%; however, in the UV region (300~400 nm), the transmission change is very drastic. This is because in the UV region, the transparent and electrically conductive ZnO thin film has the energy band gap of a semiconductor; as a result, when the energy of the incident light is greater than that of the thin film, electrons in the valence band will absorb photon energy and get excited to the conduction band having higher energy. Then, the thin-film material will absorb the photon energy of the incident light, so the optical transmission of the thin film in this region will drop steeply; this phenomenon is called optical absorption energy limitation behavior.

For specimens prepared at different pH values and before the annealing treatment, when the pH=10~10.5, the obtained ZnO membrane seemingly has transmission in the visible range higher than that of ZnO membrane prepared at PH of 10.7. However, when the pH is less than 10.5, formation of ZnO membranes is difficult, and hence, the UV-Vis spectrometer measures the transmission of the background glass substrate, which leads to an incorrect impression that the transmission reaches 90%. However, when the pH becomes 11, the transmission of the ZnO membrane shows an obvious drop mainly because of the increase in the thickness of the thin film and crystal size; therefore, we can say that pH = 10.7 is the optimal condition for membrane preparation.

Under thermal annealing, the transmission of ZnO membrane deposited on glass substrate at pH = 10.7; as can be seen that as the thermal annealing temperature is increased, the average transmission of the specimen will get improved. We conclude that this might be because the unannealed specimen still has some defects, which leads to the obvious increase in optical scattering; however, after thermal annealing, some of the oxygen atoms in the specimen penetrate the thin film to fill the oxygen vacancies, and the lattice structure is then corrected appropriately and the structural uniformity and surface flatness are enhanced. As a result, the probability of scattering of light when it passes through the specimen will be greatly reduced, and the transmission will improve considerably. Figure 6 confirms that the annealed specimens show a tendency to move toward a high-energy wavelength range in the near-UV optical absorption limit, which is caused by the phenomenon of Burstein-Moss shift[11]. Figure 6 Optical transmission of ZnO membrane measured at pH = 10.7 and annealing temperatures of 100, 200, 300, 400, 500°C; the spectral range used was 300~800 nm.

Figure 7 shows the ZnO membrane concentration and electrical mobility measured at pH = 10.7 and annealing temperatures of 100, 200, 300, 400, and 500°C. Figure 8 shows the membrane's index of refraction measured at pH = 10.7 and annealing temperatures of 100, 200, 300, 400, and 500°C. We observe that the ZnO membrane prepared at the annealing temperature of 200°C has the high concentration and low refraction. Because optical electric current increase by resulted in high concentration and low refraction, and therefore has high electric mobility.

4. Conclusion

a. The CBD method was successfully used to prepare a ZnO membrane in a chemical solution at a low reaction temperature (90°C). The addition of an appropriate amount of NH4OH to control the pH within the range 10.7~11 was useful in enhancing the thin-film thickness. Further, the deposition rate and crystal size of the membrane increased gradually with increasing pH. The obtained crystal distribution of the ZnO membrane was quite homogeneous. ZnO membrane with the increase in rapid thermal annealing temperature has the effect of enhancing the crystal to show dense microstructure.

b. It was observed that the optical transmission of the ZnO membrane prepared at pH = 10.7 and at higher annealing temperatures was better than that for membranes prepared at lower annealing temperatures. In the wavelength range of 400~700 nm, the transmission was in the range of 80~90%, and in the UV range, the optical absorption limit showed a trend of shifting toward the high-energy wavelength region.

c. A pH value of 10.7 is the optimal process parameter, which can yield a 240-nm-thick, dense, transparent, and electrically conductive membrane of ZnO.

d. The ZnO membrane prepared at an annealing temperature of 200°C has a high concentration and low refraction and therefore high electric mobility..

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Table 1 Specifications for deposition of ZnO membrane by chemical bath deposition at different pH values.

ZnAc	NH_4OH	DI Water	pH Value	Heating Time	Heating Temperature
3 ml	3 ml	74 ml	10	1 h	90°C
3 ml	5 ml	72 ml	10.3	1 h	90°C
3 ml	7 ml	70 ml	10.5	1 h	90°C
3 ml	9 ml	68 ml	10.7	1 h	90°C
3 ml	11 ml	66 ml	11	1 h	90°C

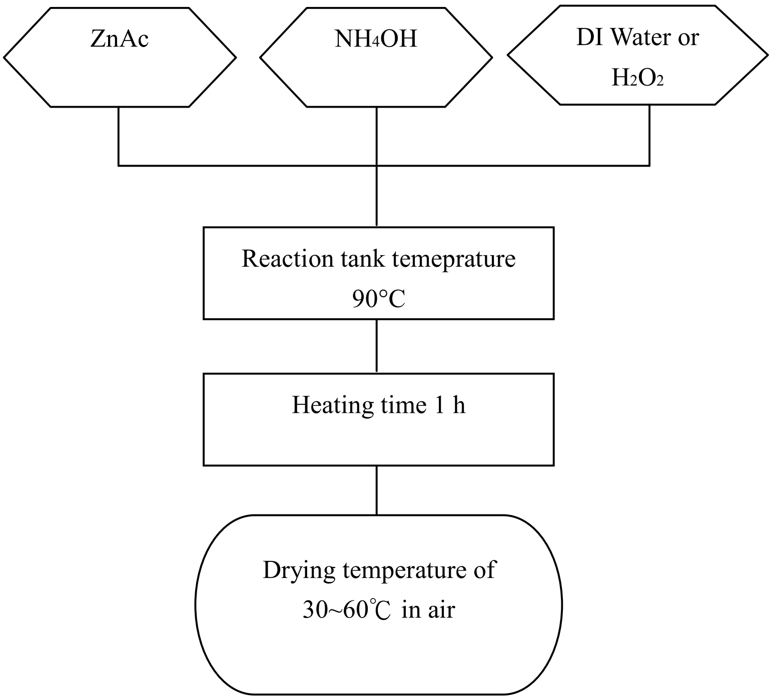

Figure 1 Flowchart of preparation process of ZnO membrane by CBD.

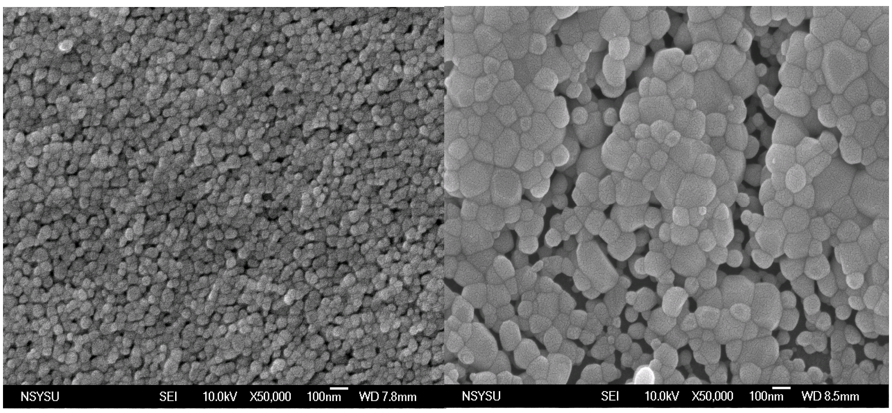

Figure 2 SEM microstructure of ZnO membrane deposited using CBD with pH values of 10.7 and 11 at an annealing temperature of 500°C.

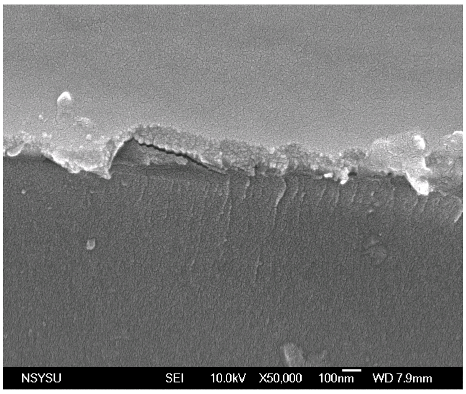

Figure 3 Cross-sectional SEM image of ZnO membrane at pH = 10.7 obtained by CBD at an temperature 500°C.

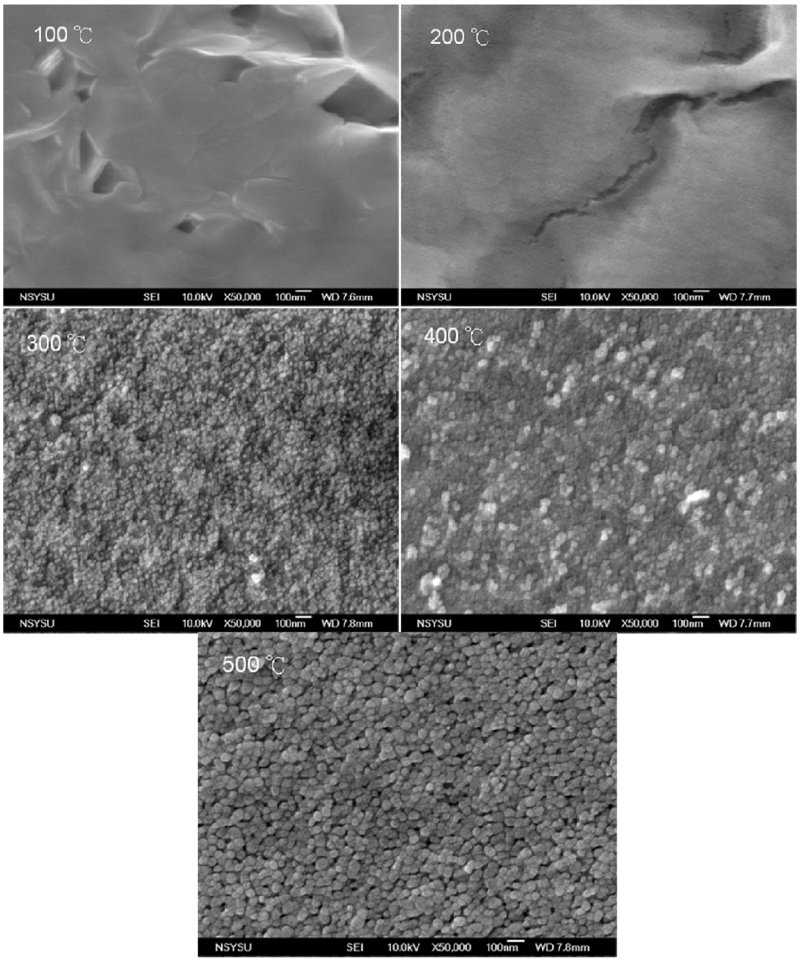

Figure 4 SEM microstructure of ZnO membrane at pH value of 10.7 and annealing temperatures of 100, 200, 300, 400, and 500°C.

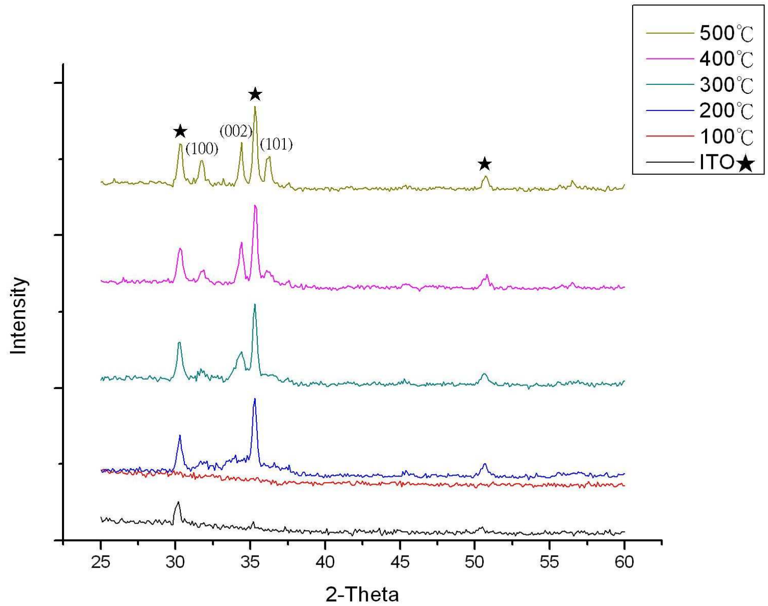

Figure 6 Optical transmission of ZnO membrane measured at pH = 10.7 and annealing temperatures of 100, 200, 300, 400, 500°C; the spectral range used was 300~800 nm.

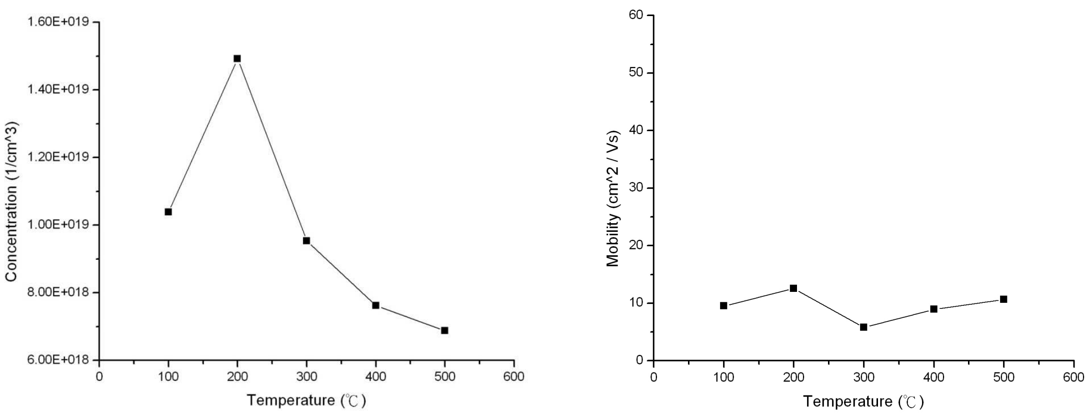

Figure 7 ZnO membrane concentration(a) and electrical mobility(b) measured at pH = 10.7 and annealing temperatures of 100, 200, 300, 400, and 500°C.

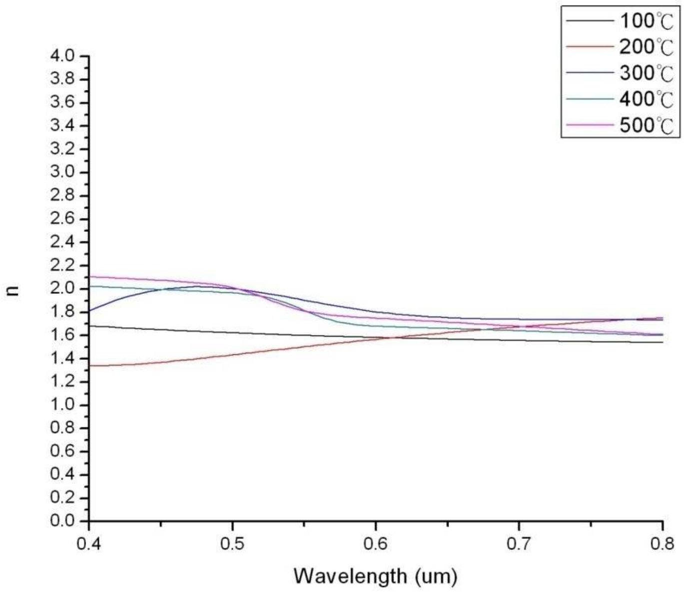

Figure 8 Index of refraction of ZnO membrane at different annealing temperatures.