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# Influence of Annealing on $Zn_{1-X}Cu_xo$ (X=6.27%) Thin Films by Sol-gel Method

Wang Xiaoyang[*,1], Ren Keming[2] and Zhou Zhen[2]

[1]*College of Mathematics and Physics, TaiZhou University, 225300, Tai Zhou, China*
[2]*College of Science, HuaiHai Institute of Technology, 222005, Lian Yungang, China*

**Abstract**: The $Zn_{1-x}Cu_xO$ (x=6.27%) films under different annealing were prepared by the sol-gel method on grass. Using the X-ray diffraction (XRD), atomic force microscopy to study the influence of annealing on the microstructure and surface morphology of the film, the result of which shows that the annealing temperature did not change the wurtzite structure of ZnO and the film density under 400 degree annealing is evened out and is the best one.In the transmission spectra of zinc oxide (ZnO) films, the transmittance in the visible light range changes little with the shift of the annealing temperature, and the absorption edge assumes a hypsochromic shift. From the point of light spectrum at room temperature, annealing temperature changes photoluminescence peak position, not significantly changing the luminescence peak position of ZnO film, but make zinc deficiency increased with annealing and the obvious enhancement in the visible region photoluminescence peak.

**Keywords:** Annealing, photoluminescence, sol-gel method, ZnO thin films.

## 1. INTRODUCTION

ZnO is a new type of photovoltaic material that is characterized by a wide energy band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV, far larger than the exciton binding energy of ZnSe (20 meV) and GaN (21 meV) [1]. Also, owing to the low growth temperatures, ZnO becomes a short-wavelength optoelectronic material having potential applications. Therefore, the research of the luminescent properties of ZnO thin films is of vital significance. With the in-depth studies of the luminescent properties of ZnO thin films, emission of blue light at various wavelengths has been reported [2-7].

The energy band gap of ZnO can be adjusted by replacing the divalent ions with cation [8], and the luminescent properties of ZnO thin films, especially purple light and blue light, can be adjusted by doping transition metal elements. Many scholars have studied the luminescent properties of Cu-doped ZnO films [9-11]. Typically photoluminescence consists of a near-UV peak at emission band of 380 nm, and the emergence of this peak has played an important role to the preparation of violet-blue shortwave devices.

In this report, we investigated the effects of annealing temperature on the sample surface appearance and luminescence properties, as well as exploring its luminescence mechanism and prepared $Zn_{1-x}Cu_xO$ (x=6.27%) thin films by using the simple sol-gel method on the glass substrates.

## 2. EXPERIMENT

### 2.1. Sample Preparation

In this experiment, the sol-gel method was employed to prepare $Zn_{1-x}Cu_xO$ (x=6.27%) thin films. Following per the stoichiometric ratio of Zn and Cu,the sol solution was prepared by mixing appropriate amounts of zinc acetate and copper acetate in 40 mL anhydrous alcohol, and adding ammonium acetate as a stabilizer for 2-hour magnetic stirring in 60 °C water area. The solution was placed quietly at room temperature for 72 hours. Then it proceeded to glass cleaning. Firstly, the substrate was rinsed with deionized water, and subjected to ultrasonic cleaning with an acetone solution for 10 min. afterwards, it was then rinsed with deionized water and then the alcohol, and finally the substrate was dried. The dried and cleaned substrate was then put on a spin coater (KW-4A). The sample rotating speed was set 3 000 rad/ min, and the sol solution after placement was dropped onto the surface of the substrate at low-speed spinning, so that the sol could be spin coated at high speed. After this spin coating step, the sol was baked in an oven at 150°C for 10 min and natural cooling. This spin coating step was repeated eight times and then annealed in a muffle furnace under different temperatures (400°C, 500°C and 600°C) respectively for 12 hours. Finally the thin film samples were obtained.

### 2.2. Characterization Analysis of the Samples

The crystalline properties of ZnO thin films were analyzed by an X-ray diffractometer with a wavelength of 0.15418 nm. The film morphology was observed by Atomic Force Microscopy Solver P47. The optical properties of the thin films were mainly studied through the transmission spectra and photoluminescence spectra at room temperature. The transmission spectra of thin films were detected by using a UV-Vis spectrometer in the measurement range of 300-600 nm. On WYF28 fluorescence spectrophotometer, the excitation light with a wavelength of 260 nm was used to test the PL spectrum samples, and the spectral wavelength ranged from 300-600 nm.

*Address correspondence to this author at the College of Mathematics and Physics, TaiZhou University, 225300, Tai Zhou, China;
Tel: 0086-0523-80769284; E-mail: 981145094@qq.com

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## 3. RESULTS AND ANALYSIS

### 3.1. Crystal Properties of thin Films

Fig. (**1**) is the X-ray diffraction pattern of $Zn_{1-x}Cu_xO$ (x=6.27%) at different annealing temperatures. As can be seen from the figure, Cu doping does not change the ZnO wurtzite structure. As can be seen from Table **1**: For the diffraction peak on (100) crystal plane, as the annealing temperature increases, the peak decreases, indicating that high temperature annealing will inhibit the grain growth on (100) crystal plane; for the diffraction peak on (002) crystal plane, as the annealing temperature increases, the peak first increases and then decreases. At this time, the (002) peak position will migrate at a large angle, and as the annealing temperature increases, the migration increases and finally stays unchanged; for the diffraction peak on (101) crystal plane, as the annealing temperature increases, the diffraction peaks increases, indicating that high temperatures will promote grain growth on (101) crystal plane. Further, the diffraction peak at 400 °C (100) has the maximum relative intensity, and the diffraction peak (101) disappears, signifying that annealing at low temperatures (400 °C) is conductive for the grain to exhibit preferred orientations on the (100) crystal plane .

**Table 1. lattice structure at different annealing temperatures**

| Samples | 2θ (002)/°C | Crystal Plane/Intensity (a.u.) | | |
|---|---|---|---|---|
| | | (100) | (002) | (101) |
| 400°C | 34.854 | 80 | 26 | 7 |
| 500°C | 34.948 | 19 | 32 | 12 |
| 600°C | 34.948 | 19 | 16 | 13 |

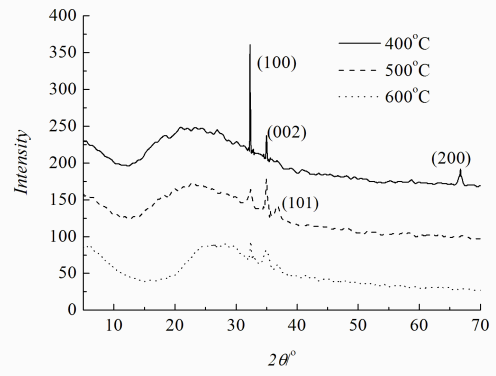
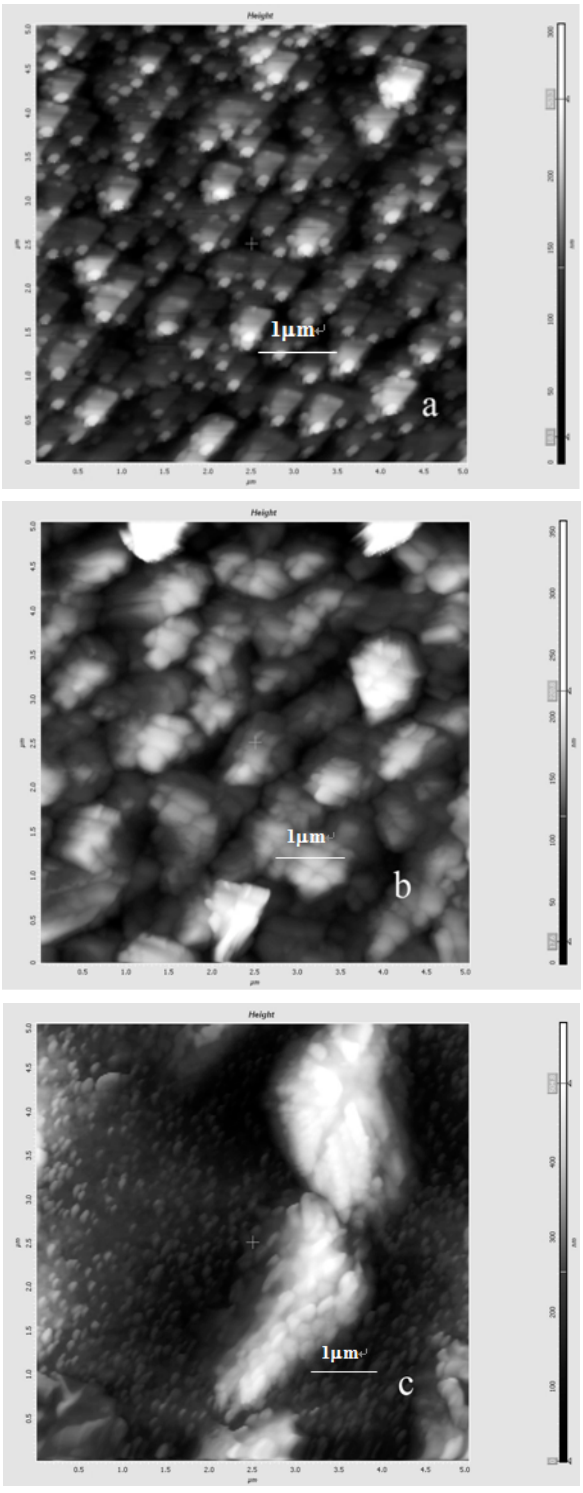



**Fig. (1).** Under different annealing temperature $Zn_{1-X}Cu_xo$ XRD (X = 6.27%).

### 3.2. Film Surface Topography

Fig. (**2**) shows the atomic force microscopy (AFM) images of $Zn_{1-x}Cu_xO$ thin films under different annealing temperatures. As can be seen from the figure, annealing temperatures exert large influences on the sample surface topography. Annealed at 400 °C, the films have a compact structure, smooth surface, good uniformity, no obvious cracks and good quality, and the grains are square. The results are consistent with XRD. Annealed at 500°C, the films have smooth surface, certain uniformity, increased surface roughness and the grains are in spherical agglomerated phase. Annealed at 600°C, the films have the same surface roughness and the grains are small sphere. The film surface uniformity is bad and the film quality becomes worse. Visibly, annealing temperatures significantly affect the thin film structure and surface topography.




a (400°C); b (500°C);c (600°C); (5 um*5 um)

**Fig. (2).** Zno: Cu AFM image.

### 3.3. Thin Film Transmission Spectrum

Annealed at different temperatures (400°C, 500 °C and 600 °C), the $Zn_{1-x}Cu_xO$ thin films prepared have the UV-VIS light transmission spectrum as shown in Fig. (**3**). From the scope of 400~600 nm (visible light), thin films have a high transmittance rate of more than 80%. With the increase of the annealing temperatures, the transmittance rate enhances. This is possibly because the light in the visible region is mainly absorbed by free carriers, while the free carriers in $Zn_{1-x}Cu_xO$ thin films have a very high migration rate, thus resulting in a very small free carrier absorption coefficient and very high transmittance rates at all visible regions [12]. In the ultraviolet region, the transmittance of thin films shows an absorption edge at about 380 nm, and the absorption edge blueshifts as the annealing temperature increases, indicating that with increasing annealing temperatures, the band gap of $Zn_{1-x}Cu_xO$ thin films decreases. In literature [13], the absorption edge of the copper-doped ZnO thin films redshifts as the annealing temperature increases. Blueshift in the absorption edge with increasing annealing temperatures still needs further research in this paper.

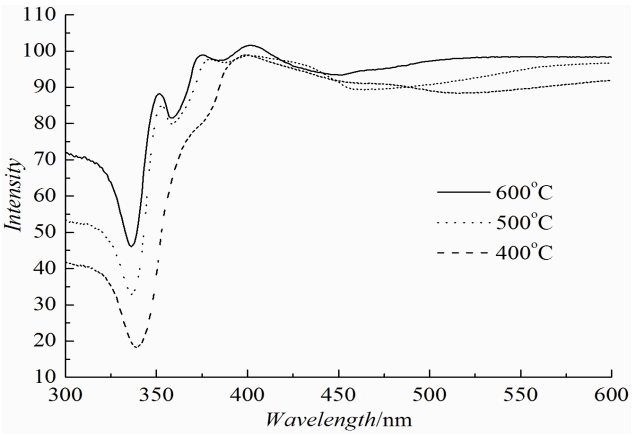



**Fig. (3).** Transmission spectrum.

### 3.4. Thin-Film Photoluminescence

Fig. (**4**) is a photoluminescence for an excitation light with a wavelength of 260 nm under different annealing temperatures. Annealed at 400 °C, the thin film's major emission peaks are located near the blue light with a wavelength of 420 nm, near the blue light with a wavelength

of 475 nm, and near the green light with a wavelength of 520 nm.

Annealed at 500 °C, the thin film's major emission peaks are located near the purple light with a wavelength of 390 nm, and other emission peaks are influenced dramatically and the intensity has increased. Under annealing at 600 °C, the purple emission peak blueshifts slightly with a wavelength of 390 nm, and other emission peaks stay unchanged and the intensity has increased.

Near-UV radiation is generally considered to be derived from the band-edge excitonic transitions [5]. Because of different annealing temperatures, changes take place in the band gap of ZnO. With the increase of annealing temperatures, the band gap decreases and the thin film samples exhibit different UV luminous intensity. This corresponds to blue shifts in the absorption edge of the transmittance spectra.

The transition multi-track method was utilized to find that the energy difference between Zinc vacancy defect level and the conduction band bottom was 2. 6 eV, and the energy difference between zinc interstitial defects and the conduction band top was 2. 9 eV, which were close to the observed blue light-emitting energy peaks at 475 nm (2. 61 eV) and 420 nm (2. 95 eV), indicating that the blue light emission of the film samples was associated with zinc defects [15]. Annealing was carried out in the atmosphere. When the oxygen content was not high, there may easily be some zinc deficiencies. As the annealing temperature increases, a part of Zn atoms deviated from the lattice and formed Zn defects, leading to increased number of Zn defects and resulting in the growing emission intensity of blue light.

For green light emission peak near 520 nm, some literature suggests that it is due to the transition of defect levels when electrons at the bottom of the conduction substituted Zn [14]. By XRD and atomic force microscopy, it can be seen that with increasing annealing temperatures, the thin film had deteriorated uniformity and increased defects, which might lead to incremental green peak intensity with an increase in the annealing temperature.

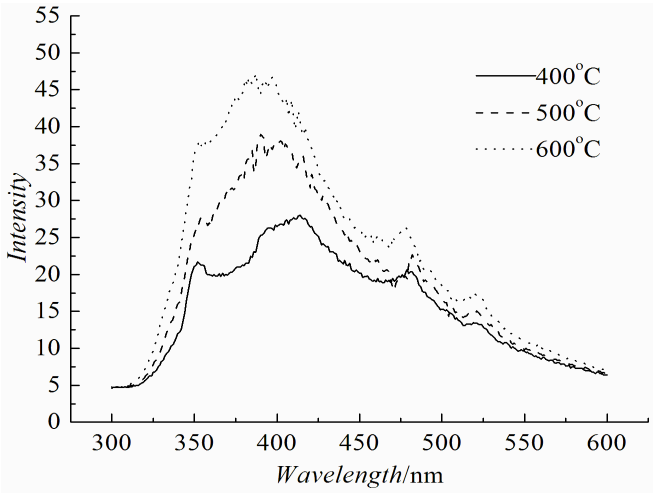



**Fig. (4).** Photoluminescence spectrum.

## CONCLUSION

The sol-gel method was employed to prepare $Zn_{1-x}Cu_xO$ (x=6.27%) thin films under different annealing temperatures, and its structure and optical properties were studied. As per XRD and AFM test results, annealed at 400 °C, the films had a compact structure and good uniformity, presenting (100) orientations. In the visible light range, thin films had a high transmittance rate of more than 80%. With the increase of the annealing temperatures, the transmittance rate of ZnO thin films changed little. In addition, the absorption edge blueshifts, showing that the band gap decreases due to annealing. In terms of the PL spectrum at room temperature, it can be seen that annealing only change the position of the band-edge emission peaks without changing the peak position of other emission peaks in the thin films. However, the intensity of the emission peak is greatly influenced by annealing. With the increase of the annealing temperatures,

both blue and green emission peaks have enhanced intensities. Blue emission peak is enhanced probably because of more new defects generated by annealing in the atmosphere, while green emission peak is enhanced probably because of more defects in the thin films incurred by increased annealing temperature.

## CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

## ACKNOWLEDGEMENTS

Declared none.

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