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Article

Electrical Properties of CZO Films Prepared by Ultrasonic Spray Pyrolysis

Lung-Chien Chen [1,*], Cheng-An Hsieh [1], Xiuyu Zhang [1] and Jhih-Ci Jhen [1]

1 Department of Electro-Optical Engineering, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao E. Road, Taipei 106, Taiwan;
E-Mails: ocean@ntut.edu.tw; t102658033@ntut.edu.tw; zxy.1013@live.com;
t101658067@ntut.edu.tw

* Department of Electro-Optical Engineering, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao E. Road, Taipei 106, Taiwan; E-Mail: ocean@ntut.edu.tw;
Tel.: +886-2-2771-2171-4634; Fax: +886-2-8773-3216.

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Abstract: Recently, CuZnO (CZO) films attracted more and more attention because of its great potential application in semiconductor devices. ZnO shows n-type conductivity and several elements have been tried to dope in ZnO to improve the electrical properties. This study focused on the transition of the electrical properties of CZO films, and find out at which concentration the conductivity of CZO films will from n-type to p-type. In this study, CZO films were fabricated by ultrasonic spray pyrolysis with copper acetate, zinc acetate, and ammonium acetate precursor solution. The concentration of Cu ions in the CZO films were changed by the concentration ratio between copper acetate and zinc acetate in precursor solutions. Additionally, these samples are measured by Hall Effect measurement, X-ray diffraction analysis, transmittance measurement and photoluminescence measurement. The result shows that when the concentration of copper ions in CZO films at 5%, the conductivity of the CZO films will turn from n-type to p-type.

Keywords: Conductivity properties, CZO, p-type

1. Introduction

Zinc oxide (ZnO) is a popular material because of the large band gap (3.4eV) and large exciton binding energy (60 meV) [1-2]. It has wildly used in laser devices, gas sensor, ultraviolet¬visible light emission devices and many other application [3-6].

ZnO shows n-type conductivity and several elements have been tried to dope in ZnO to improve the electrical properties, such as Cr, Co, Ni, Mn or Fe ion [7-12]. This study is focus on the Cu-doped ZnO because of its great potential application in semiconductor devices. These days, doping Cu atoms attracted more and more attention due to the characteristic of having no clustering tendency and the secondary phases of Cu and copper oxides (Cu2O and CuO) are not ferromagnetic (FM) [13].

It is important to know the properties of CuZnO (CZO) thin films, this study investigated the CZO thin films by doping different concentration of Cu from 0% to 6%. CZO thin films were fabricated on glass substrates using ultrasonic spray pyrolysis, these samples are measured by Hall Effect measurement, X-ray diffraction analysis, transmittance measurement and photoluminescence measurement.

2. Results and Discussion

2.1. Morphological and structural properties

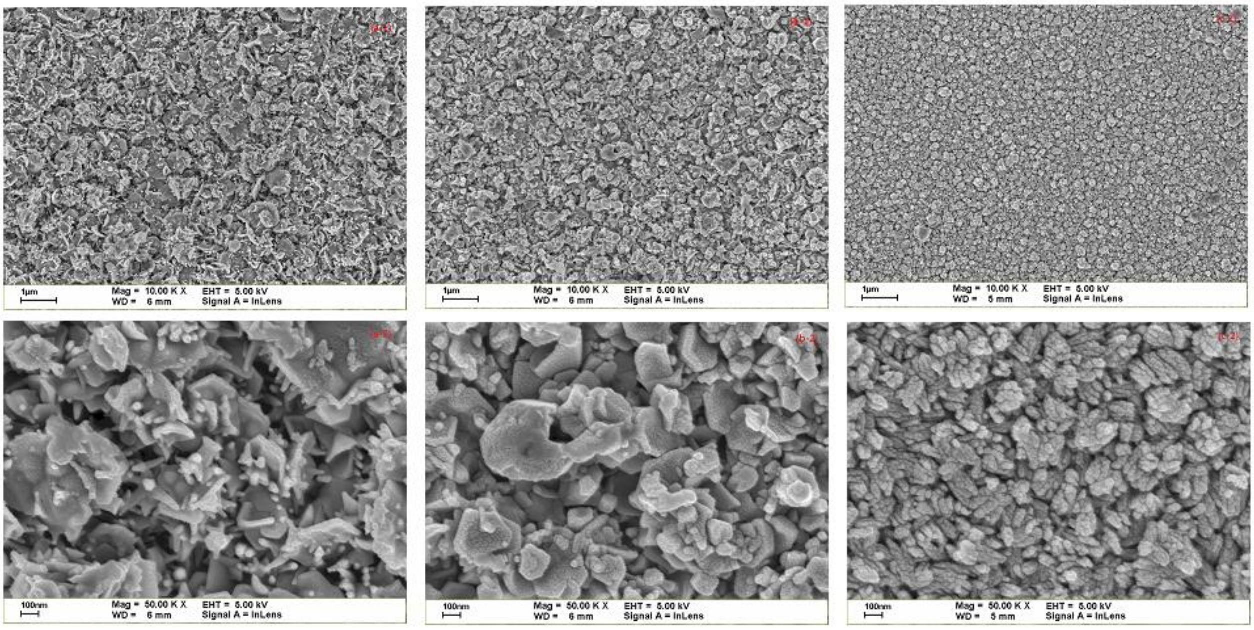

Fig. 1. (a) SEM image of the $Zn_{0.98}Cu_{0.02}O$. **(b)** SEM image of the $Zn_{0.96}Cu_{0.04}O$. **(c)** SEM image of the $Zn_{0.94}Cu_{0.06}O$.

Figure 1 shows the surface morphologies of CZO thin films at different concentration. As seen, with the Cu concentration increased, the films have tightly packed grains and a relatively smooth surface.

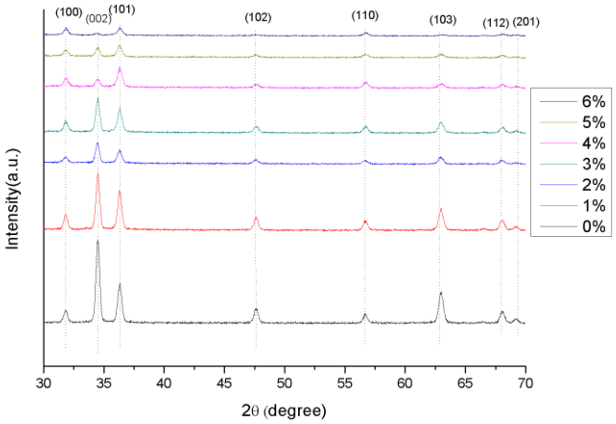

Fig. 2. XRD curves of $Cu_xZn_{1-x}O$ {x = 0 ~ 0.06}.

Figure 2 shows XRD curves of different Cu concentration samples, the diffraction peaks corresponding to ZnO (002) are observed. The intensity of the ZnO (002) peak is clearly decreased with increasing Cu concentration. It is seem that doping Cu will decrease the crystallinity as compared to pure ZnO films. Table 1 shows Hall-effect measurements of CZO thin films. As seen, natural ZnO thin film is n-type, when the concentration of Cu increased to 5%, CZO thin film changed from n-type to p-type.

Sample	Mobility (cm^2/V-s)	Concentration (cm^{-3})	R_0 (Ω-cm)	Conductivity
ZnO	6.96	$-1.347e^{+17}$	6.66	n
$Cu_{0.03}Zn_{0.97}O$	1.06	$-2.599\ e^{+17}$	22.76	n
$Cu_{0.04}Zn_{0.96}O$	0.79	$-3.016\ e^{+18}$	2.619	n
$Cu_{0.05}Zn_{0.95}O$	0.692	$+5.517\ e^{+18}$	1.634	p

Table 1. Hall-effect measurements of CZO thin films.

2.2. Transmission and Absorption

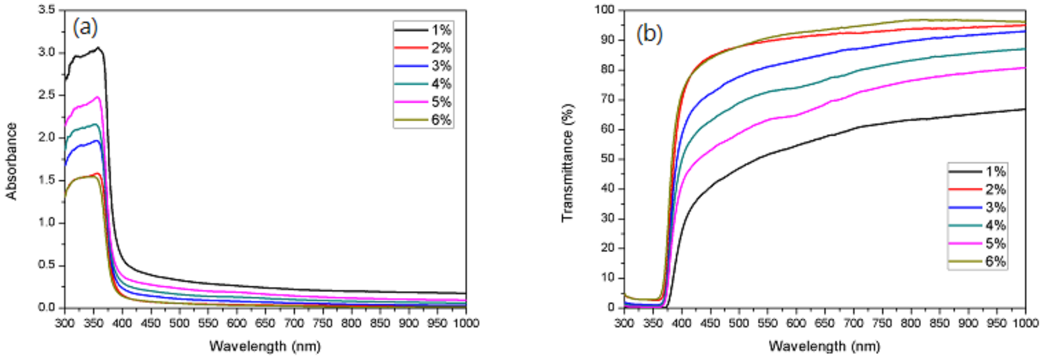

Fig. 3. (a) Absorption curves and (b) Optical transmittance spectra.

The results of UV-Visible transmittance and absorption measurements are shown in figure 3. Figure 3(a) shows that the sharp ultraviolet absorption edges of all CZO films are in the range between 385 – 410 nm. The band gap of CZO films from 1% to 6% is 3.02 eV ($Cu_{0.01}Zn_{0.99}O$), 3.06 eV ($Cu_{0.02}Zn_{0.98}O$), 3.09 eV ($Cu_{0.03}Zn_{0.97}O$), 3.11 eV ($Cu_{0.04}Zn_{0.96}O$), 3.18 eV ($Cu_{0.05}Zn_{0.95}O$) and 3.22 eV ($Cu_{0.06}Zn_{0.94}O$), respectively. It shows when the Cu concentration increased, the energies of the absorption edge are higher. From figure 3(b), it shows that the transmittance of the films in the visible region is above 40%.

2.3. Raman analysis

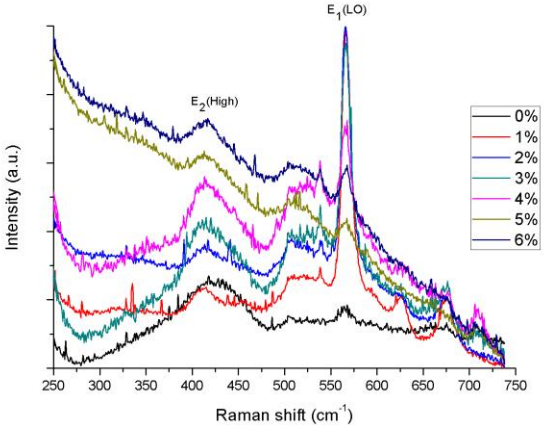

Fig. 4. . Raman spectra of $Cu_xZn_{1-x}O$ {x = 0 ~ 0.06}

Figure 4 shows the room temperature Raman spectra of CZO thin films. It shows the influence of Cu-doping in ZnO structure. As seen, the intensity of E_2 peak is higher with increasing the Cu concentration. It also shows the peak are shifted from 425 cm^{-1} to 415 cm^{-1} compare to the ZnO thin film, this frequency shift was caused by the lattice defects and lattice disorder [14-15]. The peak at about 566 cm^{-1} can assigned to E_1 longitudinal optical (LO) mode [E_1(LO)], which caused by some defects of oxygen vacancy and Zn interstitial [16-18].

2.4.Photoluminescence

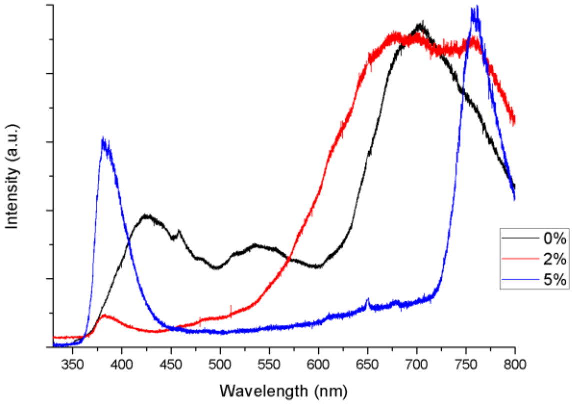

Fig. 5. Photoluminescence spectra of $Cu_xZn_{1-x}O$ {x = 0, 0.02, 0.05}

To investigate the quality and the wavelength emission change with the Cu concentration the photoluminescence study was taken. Figure 5 shows the photoluminescence spectra of CZO thin films. The peak at 424 nm is attributed to the wurtzite structure of ZnO. With Cu-doping, the peak shifted and has an ultraviolet emission at 380 nm, it is attributed to the near band-edge free-exciton transition [19-20]. This is in good agreement of the absorption edge shifts with increasing Cu concentration. As seen, there is also a broad yellow-red emission from 600 nm to 750 nm [21], which is due to copper impurities or oxygen vacancies. There are many intrinsic or extrinsic defects have been reported in the visible region, such as antisite oxygen, surface defects and zinc vacancies [22-24].

3. Experimental Section

In this sturdy, CuZnO (CZO) thin films were fabricated on glass substrates using ultrasonic spray pyrolysis with copper acetate [Cu(CH3COO)2 • H2O], zinc acetate [Zn(CH3COO)2 • 2H2O], and ammonium acetate [CH3COONH4] precursor solution. A mixture of copper acetate, zinc acetate and ammonium acetate powders were used to prepare the solution. The mole ratio of copper acetate mixed zinc acetate to ammonium acetate maintained 1:3. In the mixed powder of copper acetate and zinc acetate, the mole concentration of copper acetate were changed from 0 to 0.06. The powders were put in 20ml pure water, after mixing the powder by magnetic stirrer with 1 hour, CZO thin films were fabricated by using ultrasonic spray pyrolysis in 500℃ for 15 minutes.

4. Conclusions

In this study, different concentration of CZO thin films are investigated. CZO thin films will change from n-type to p-type when Cu-doped at 5%. The band gap of CZO films are increased from 3.02 eV ($Cu_{0.01}Zn_{0.99}O$) to 3.22 eV ($Cu_{0.06}Zn_{0.94}O$). In Raman spectra, the intensity of E_2 peak is higher with increasing the Cu concentration, and the peak are shifted from 425 cm^{-1} to 415 cm^{-1} compare to the ZnO thin film. In photoluminescence spectra, the peak shifted with increasing Cu concentration.

Acknowledgments

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Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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