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Properties and Synthesis of CuZnO films prepared by Ultrasonic spraying

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ABSTRACT

Cu-doped ZnO (CZO) films have been prepared on glass substrate by ultrasonic spray method using zinc acetate, copper acetate and ammonium acetate aqueous solution as precursors. The X-ray diffraction analysis and field emission scanning electron microscopy were used to investigate the composition and the morphology of the films. Transmission measurement in visible light showed a decrease trend from pure ZnO to pure CuO as Cu content increased. Photoluminescence measurement was also used to research the optical properties of the films. Electrical properties were investigated by Hall measurement, which indicated that the films have higher resistivity, higher mobility, and lower carrier density than that of pure ZnO and CuO films.

1. INTRODUCTION

Zinc Oxide (ZnO) is a wide direct bandgap (3.36eV) II-VI compound semiconductor, which has a large exciton binding energy of 60mV with a hexagonal wurtzite structure (Chen 1998). These properties enable ZnO a promising material for short wave-length optoelectronic applications, such as light emitting diodes, thin film transistors, gas sensors, ultraviolet detectors, and lasers (Guo 2001, Masuda 2003, Comini 2006, Liu 2000, Service 1997, Willander 2009). On the other hand, copper oxide is one kind of semiconductor with a band gap of 1.4eV (Ghijsen 1988) and absorbs strongly in visible spectrum. It has been investigated for applications in many fields, such as gas sensors, solar cells and so on (Yoon 2000, Singh 2011, Hiroki 2012). In general, many researches have studied in small amount of Cu incorporated into ZnO. Most of these researches focused on the changes in physics properties between doped materials and pure ZnO (Mishra 1990, Xu 2004, Wang 2005, Ai 2012, Rishikeshi 2012, Song 2012, Sung 2012). Others showed applications in gas sensors and solar cells of this CZO material (Yoon 1998, Muhamad 2008, Sharma 2009, Benjamin 2009, Rahmani 2009, Ma 2012, Chow 2013). There are few papers reported to discuss the physical properties of the composite material that is combined by ZnO and CuO. (Rahman 2011) have reported chemical sensor applications of CZO nanostructured materials, which indicate

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that the CZO nanostructured materials have a promising application in future semiconductor devices.

In this study, ultrasonic spray method is employed to prepare CZO films with different ratios of Cu and Zn and the structures, morphologies, and properties were measured by various techniques. The ultrasonic spray method was used because it has the the advantage of high growth rate, large area uniformity, and inexpensive preparation (Lu 2002). The structure and the properties of the CZO films changes when the ratio of Cu to Zn changed. When the proportion of the Zn is higher than that of Cu, the properties of the CZO film are similar to the pure ZnO film. On the contrast, when the proportion of Cu is higher, the film properties are much more like the CuO film.

2. EXPERIMENTAL DETAILS

CZO films were deposited by ultrasonic spraying technique at atmospheric pressure on a glass substrate. Before deposition, the glass substrates were first cleaned in Acetone and Methanol. Then the substrates were rinsed in de-ionized water and dried in the flowing Nitrogen. To obtain the precursor solution, three kinds of aqueous solution, zinc acetate, copper acetate and ammonium acetate were chosen as the sources of zinc, copper and nitrogen respectively. The molar concentration of zinc acetate and copper acetate solution were adjustable because the ratio of Cu to Zn in the CZO films was controlled by the ratio of copper ions and zinc ions in the precursor solution. The sum of the molar concentration of these two solutions was 0.15M and the ammonium acetate solution were fixed at 0.45M. Five different ratios were set in the experiment. Samples referred to as CZO1, CZO2, CZO3, CZO4 and CZO5 were made from precursor solutions with relative Cu and Zn contents as follows: [Zn]1, [Cu]0.25[Zn]0.75, [Cu]0.50[Zn]0.50, [Cu]0.75[Zn]0.25 and [Cu]1, respectively. The solutions were stirred at room temperature for 1h and then moved into a commercial ultrasonic nebulizer where makes the solutions be aerosol. The aerosol was transported to the substrate by high-purity nitrogen gas and the substrate was kept at 500°C. The deposition time lasts for 15 minutes and the thickness of the films were about 500-800nm.

The crystalline microstructure of the films were determined by X-ray diffraction with Cu-K_α radiation (λ=0.1541nm) in the scanning range between 2θ=20° and 60°. Surface morphology was studied by a LEO1530 field emission scanning electron microscope. Optical transmission properties were measured in the range of 300-1100nm using by a Hitachi U-2001 Ultraviolet-Visible spectrophotometer. Photoluminescence (PL) spectra were excited by a He-Cd laser (325nm) and collected by a Dongwoo spectrophotometer. The test of electrical properties including resistivity, carrier concentration and Hall mobility were measured by a Hall effect measurement system using the van der Pauw method.

3. RESULTS AND DISCUSSION

3.1 Crystalline structure

Fig.1 shows the XRD patterns of CZO films deposited on glass substrates. For CZO1 film (pure ZnO), the diffraction peaks were observed at 2θ=31.86°, 34.57°,

36.39° , 47.66° and 56.71° , which can be corresponded to (1 0 0), (0 0 2), (1 0 1), (0 1 2), and (1 1 0) planes of ZnO phase. This result showed the thin film was polycrystalline and had a hexagonal wurtzite structure. For CZO5 film (pure CuO), the peaks at 2θ=32.59° , 35.60° , 38.76° , 48.95° , 53.65° , and 58.30° corresponding to (1 1 0), (1 1 -1), (1 1 1), (2 0 -2), (0 2 0), and (2 0 2) planes of CuO with monoclinic structure. The peaks observed above are fully matched with the hexagonal wurtzite structure ZnO (JCPDF # 75-0576) and monoclinic structure CuO (JCPDF # 89-5895). From Fig.1 it is evident that the peaks belonging to ZnO decrease and peaks from CuO increase with the increasing relative Cu concentration in precursor solutions.

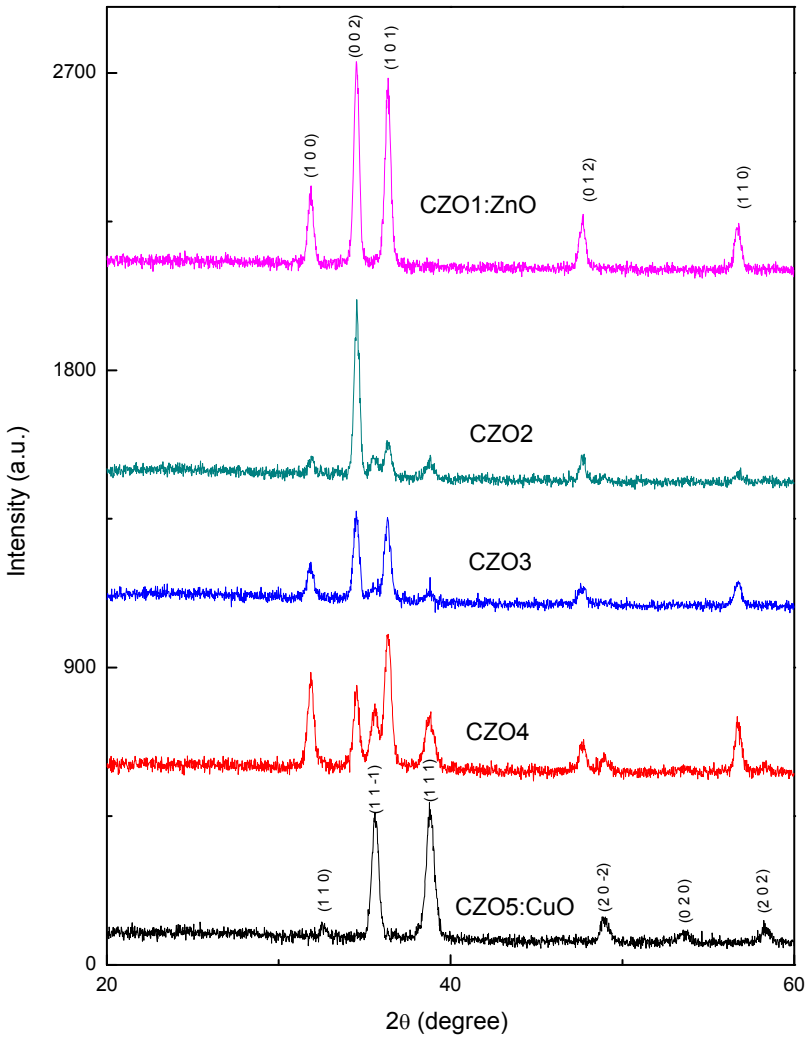

Fig. 1 XRD patterns of different concentration of CZO thin films

Fig. 2 depicts the field emission scanning electronic microscopy (FESEM) image of the surface morphology of CZO films were observed. As shown in the figure, the morphology changes greatly with the variation from ZnO to CuO. CZO2 and CZO4 films formed small island structure with about 1 micrometer diameter on the films. Other films showed smoother morphology with smaller grains and no island structure. There are many parameters influencing the morphology structure formation, such as the molar concentration and the ability to be aerosol of the precursor aqueous solution. Different ratios of precursor aqueous solutions also have different ability to be vibrated to aerosol. Due to the great change in ratios of precursor solutions, it can explain why there is such a great change in the morphology structures among these films.

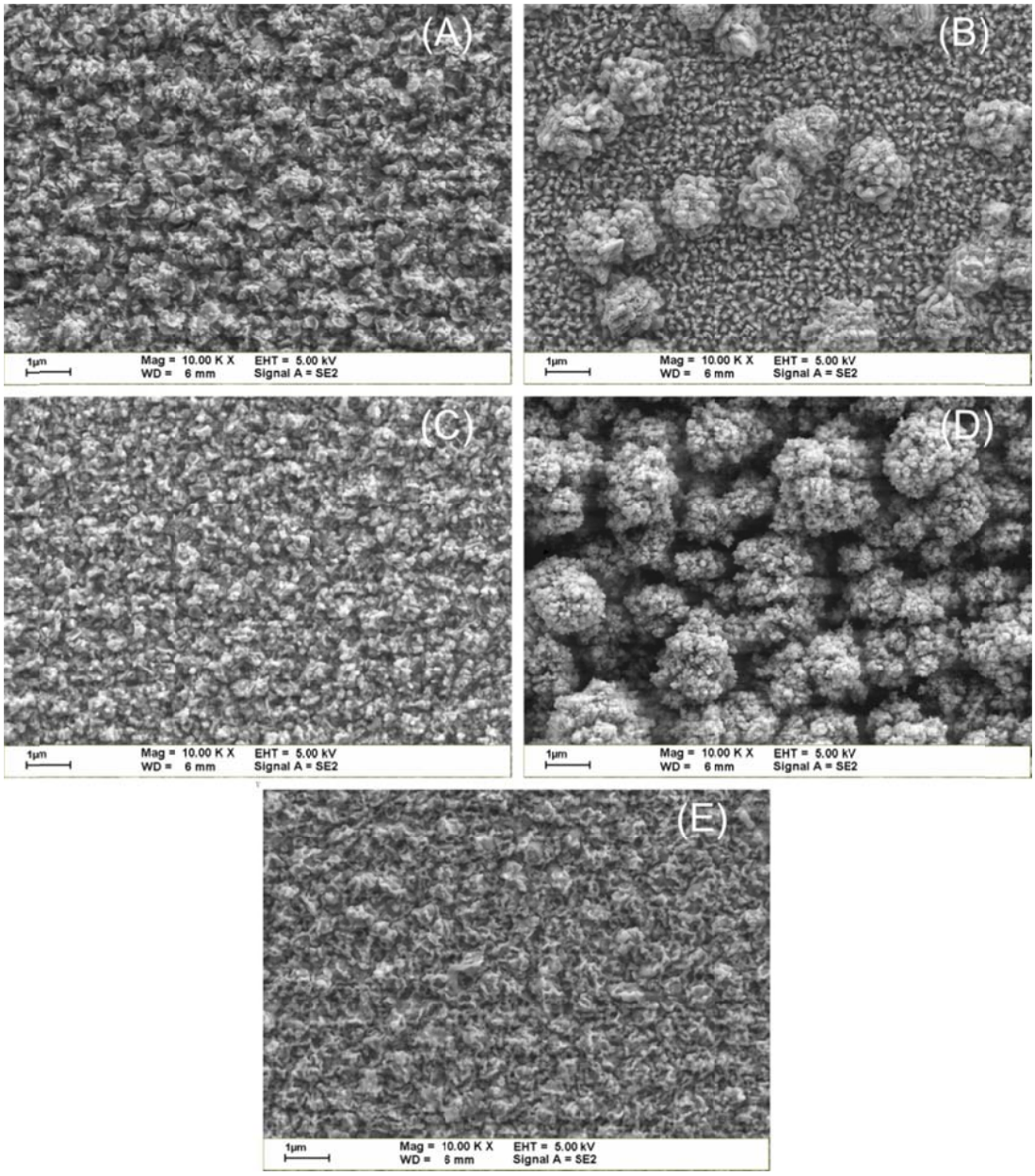

Fig. 2 FESEM image of CZO films. (A) CZO1, (B) CZO2, (C) CZO3, (D) CZO4, and (E) CZO5.

3.2 Optical characteristics

The optical transmission spectra of CZO films are shown in Fig. 3(A). It can be observed that CZO1, CZO2, and CZO3 films have the quite similar transmission properties. The transmission spectrum of CZO1 film is the property of ZnO, which has a high transparency in the visible range. Due to the concentration ratio of Cu to Zn is less than 1 in CZO2 and CZO3 films, there are more proportion of ZnO than that of CuO in the films, which leads to the result that these two films has a similar transmission property to the ZnO film. The CZO4 film has similar transmission spectrum to CZO5 (CuO) film because of the high concentration of CuO in the film and the films (CZO4 and CZO5) have strong absorption in visible region. Furthermore, the average transmittance in the visible region of all films is shown in Table 1. The average transmittance of films decreases from 67.9% to 0.28% due to the concentration of CuO in the films increasing.8

The direct optical band-gap E_g of CZO films as shown in Table 1 was obtained from the transmission spectra using the following relationships:

$$\alpha d = -\ln T \tag{1}$$

$$\alpha^2 = A\left(hv - E_g\right) \tag{2}$$

where α is the absorption coefficient values; d is the film thickness; T is the transmittance spectra of thin films; A is a constant; hv is the photon energy and E_g is the optical band-gap of the semiconductor.

The graph of α^2 versus hv plots for CZO films are shown in Fig. 3 (B and C). It can be seen that the extrapolation of linear portion of the graph to energy axis at α^2=0 gives the E_g value. The optical band-gap of all films are shown in Table 1 and the variation is plotted in Fig. 3(D). It also can be observed that the optical band-gap has a decrease trend when the Cu concentration increases in the films. Because of the similar transmission properties of CZO1, CZO2, and CZO3 films, these three films also have a close optical band-gap. Of all the three films, CZO2 has a higher optical band-gap. Due to the CuO phase in the film, the optical band-gap should be decreased in reasonable. This abnormal increase of optical ban-gap may attribute to the thinner thickness of the CZO2 film than that of CZO1 film. (Bachari 1999) have reported the similar results. In UV region, the sharp absorption can be observed, and the absorption increases with an increase of film thickness. The absorption edge gradually shifts to higher wavelength range with increase in thickness, which is consistent with the results reported by previous literatures (Lin 2004). It is observed from Fig. 3(D) that for all the films prepared, there is a decrease trend of the optical band-gap as the CuO concentration growing in the films.

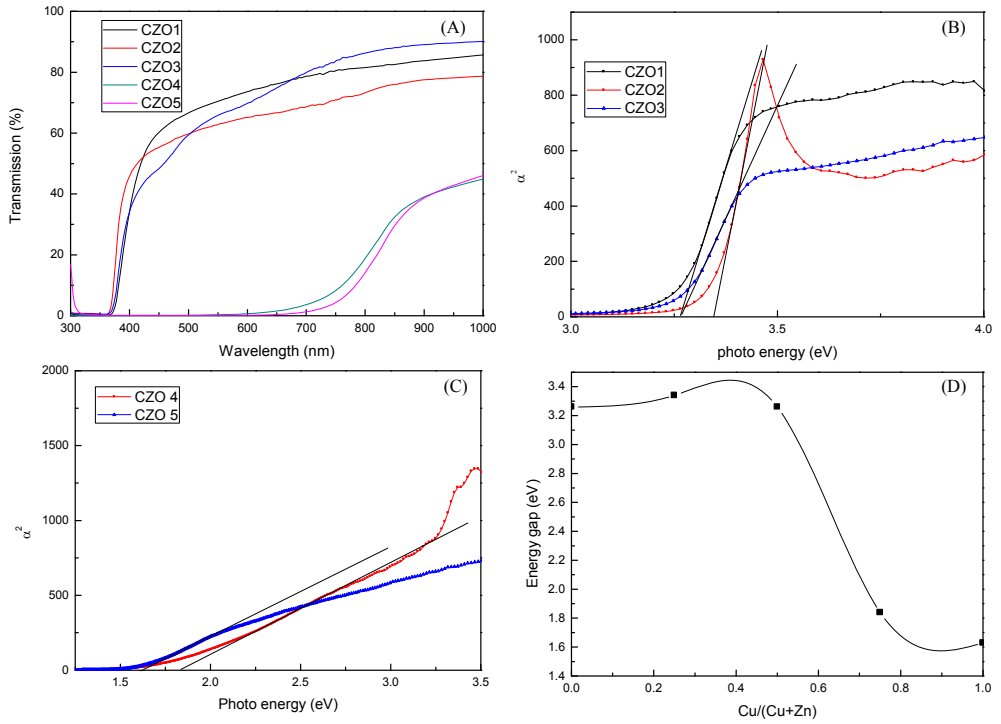

Fig. 3 Transmission properties and variation of the CZO films: (A) optical transmission spectra of the CZO films, (B) the graph of α^2 vs. hv plots for CZO1, CZO2, and CZO3 films, (C) the graph of α^2 vs. hv plots for CZO4 and CZO5 films, (D) variation of optical band-gap E_g of the CZO films when the Cu concentration in the films increases.

Table 1 Thickness, average transmittance in visible region and optical band-gap of CZO films.

	Thickness (nm)	Average transmittance in visible region (%)	Optical band-gap (eV)
CZO1	850	67.9	3.26
CZO2	510	66.4	3.34
CZO3	640	62.8	3.26
CZO4	800	0.74	1.84
CZO5	820	0.28	1.63

Photoluminescence (PL) measurement of the CZO films was carried out to gather further information of optical properties. Fig. 4 shows the PL spectra of the films. The peaks of ZnO film was indicated at 430nm and 760nm. Many groups have reported that different defect centers in ZnO are responsible for the peaks observed. (Ahn 2009) reported that the violet emission at 430 nm is due to the interstitial znic (Zn_i). (Cross 2005) postulated that the near-IR emission at about 760nm originates from defects similar to those responsible for the red emission in ZnO, i.e. oxygen-related defects. In this case, the peaks observed from ZnO are defect emission. The pure CuO film showcase no ZnO near band edge emissions and a new emission peak centered at

about 760nm can be seen, which has been observed by (Carglar 2012) in their research. The CZO2 sample showed new emission peaks centered at about 520nm and 690nm. These emissions were also observed by (Soomro 2012) in their research article and are attributed to the transition from Zn_i to valance band. The CZO3 and CZO4 films showed no emission peaks at wavelength lees than 600nm. That may be caused by the decrease concentration of ZnO in the films. Furthermore, strong emissions at 625~760 nm can be observed. The emissions may be consisted of the defected ZnO emission and CuO emission so that have a higher intensity. Compared with the spectra of these films, the CZO films exhibits a photoluminescence properties that is combined by ZnO and CuO properties.

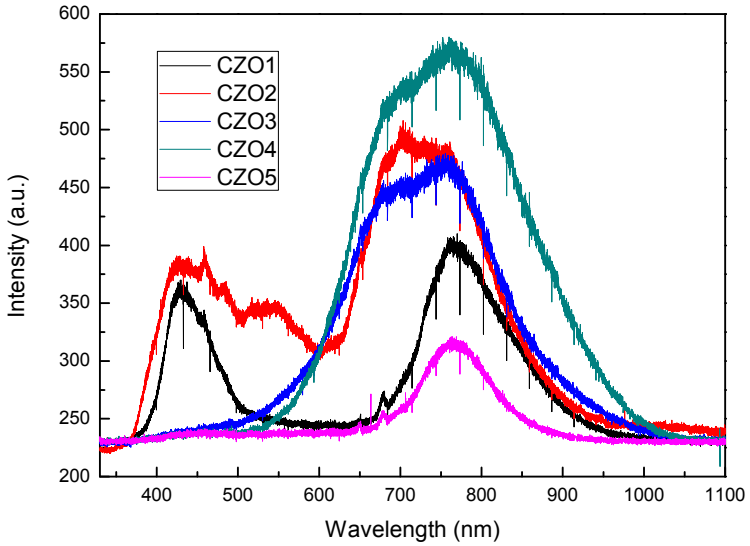

Fig. 4 Room temperature PL spectra of CZO films.

3.3 Electrical properties

The electronic characteristics of all the films were measured by a Hall Effect measurement system and the results are shown in Table 2. The failure of measuring the CZO2 and CZO3 films may be attribute to the high resistivity of the films and the measurement limitation of the measurement system. The CZO1 film, known as pure ZnO film, which has nitrogen doped, showed p-type conductivity is corresponding to earlier research by (Lu 2002). Because the ZnO and CuO films are both p-type, it can be inferred that the CZO films prepared should be also p-type. It is be confirmed by the statistics of CZO4 film in Table 2. Compared with the statistics in Table 2, it can be find that the CZO4 film has a higher resistivity and mobility, lower carrier concentration than pure ZnO and CuO films. That means the CZO films has worse conductivity than pure ZnO and CuO films. This result may ascribe to the defect in the films cause by the combination of different structure materials.

Table 2 The electronic properties of CZO films

	R_0 (Ωcm)	p_s (cm^{-3})	μ (cm^2/Vs)
CZO1	0.02	2.65×10^{20}	1.25
CZO4	358.01	8.38×10^{15}	2.08
CZO5	7.11	8.59×10^{18}	0.10

4. CONCLUSION

The structural, morphological, optical and electronic properties of the CZO films prepared by ultrasonic spray method were investigated. The XRD patterns showed that the films are polycrystalline and revealed the ZnO phase and CuO phase variation in these films. CuO phase doped into ZnO film caused great change of the morphology of the films prepared. The transmission measurement related to the optical band-gap of the films showed decrease trend in visible region as expect and the optical band-gap too. The CZO composite films showed both ZnO and CuO photoluminescence features. In addition, with CuO incorporate into films, the electronic properties, including resistivity and carrier concentration, gets worse. All these properties indicates the CZO films have potential application in solar cell, light emitting diode, and some other semiconductor devices.

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