Research Article

The Influences of CuO/ZnO Ratios on the Crystallization Characteristics Electrical and Magnetic Properties of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ Powders

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This study synthesizes $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders using an aqueous solution method. The $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders with different content ratios of CuO and ZnO ($\text{CuO}:\text{ZnO} = 1:2, 1:1, \text{ and } 2:1$) were formed. The crystalline characteristics and electrical and magnetic properties depended primarily on the mixing effect and oxygenation. The electrical resistance of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ ($1.5 \times 10^5 \Omega/\square$) powder was lower than that of CuO ($5.82 \times 10^5 \Omega/\square$) powder after ZnO mixing in CuO. This reduction was attributed to the substitution of Cu^+ ions at Zn^{2+} sites or the formation of electron trapping defect centers. The concentration ratio of Cu_2O phase in $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powder mainly dominated the electrical resistance. The $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ has a diluted ferromagnetism (DFM) and paramagnetism (PM). The electrical resistance of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ decreased; the magnetic behavior increased instead. This study also analyzes the chemical binding of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powders to confirm the contribution of Cu^+ ions to the electrical and magnetic properties.

1. Introduction

Metal oxide nanostructures, such as ZnO [1], CuO [2, 3], SnO_2 [4], In_2O_3 [5], and TiO_2 [6], have attracted extensive attention for their optical, electrical and magnetic properties. They are widely applied in various optoelectronic devices, such as photocatalyzers [7], solar cells [8], photodiodes [9], and humidity sensors [10].

Recent reports on CuO-ZnO compound and CuO/ZnO heterojunction structures show the need for efficient characteristics [11, 12]. A few Cu dopants (<10 at.%) doped ZnO samples have been investigated [13, 14]. However, the effects of the higher Cu doping contents (>10 at.%) on

electrical properties and magnetic behavior of ZnO were rarely reported. Thus, the electrical properties that dominate devices performance and the influences of higher dopant level on the electrical resistance of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ are topics worthy of further research. In addition, ZnO-diluted magnetic semiconductor (DMS) can enhance its magnetic behavior by Cu doping [15]. The influences of high CuO concentration on magnetic properties of ZnO are not clear.

The study uses an aqueous solution method to synthesize CuO and $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders. Specifically, this study examines the effects of high ZnO content mixed with CuO on the structural, electrical, and magnetic properties of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders. The relation of electrical resistance and

FIGURE 1: DSC-TGA curve of CuO.

magnetic properties for $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders was carried out to understand the influences of CuO mixing effects and clarify the contribution of CuO and Cu_2O phase.

2. Experimental Procedures

The experiments in this study synthesized the CuO powder using an aqueous solution. To acquire the CuO powder, 0.25 M copper acetate [$\text{Cu}(\text{CH}_3\text{COO})_2$] was synthesized in deionized water. The precursor solution was uniformly stirred at 80°C for 1 h and then dried at 120°C in an oven to evaporate the solvent. The resulting powder was then analyzed by a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA) to determine the thermal properties of fabricated CuO nanoparticles. The DSC and TGA results indicate that CuO powder could be obtained after thermal annealing in a furnace for 1 h. For $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders, the copper acetate and the zinc acetate were mixed with different ratios ($\text{CuO}:\text{ZnO} = 1:2, 1:1$ and $2:1$) and the molar ratio of zinc acetate to citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was 2. The $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders were then designed according to the concentration ratio of CuO and ZnO as $\text{Cu}_{0.3}\text{Zn}_{0.67}\text{O}$, $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$, and $\text{Cu}_{0.67}\text{Zn}_{0.3}\text{O}$.

This study investigates the structural characteristics of powders using X-ray diffraction (XRD, Siemens/D5000) and scanning electron microscopy (SEM, Hitachi/S-4100). To understand the contribution of CuO on the electrical and magnetic characteristics of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders, a semiconductor parameter analyzer (Agilent/4155-B) and superconducting quantum interference device vibrating sample magnetometer (SQUID VSM) were used, respectively. The composition and chemical bonding of the crystallization were analyzed using an electron spectroscopy for chemical analysis (ESCA, PHI 5000 VersaProbe).

3. Results and Discussions

This study uses DSC and TGA analysis to determine the crystallization conditions of CuO precursors (Figure 1). The

FIGURE 2: XRD patterns of (a) as-grown CuO powder and CuO powder with annealed temperature of 500°C. (b) $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ ($x = 0, 0.33, 0.5, 0.67$, and 1) powders.

FIGURE 3: Morphology of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders: (a) $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$, (b) $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$, and (c) $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$.

FIGURE 4: Magnetic field dependence of magnetization (M - H) for $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders at 10 K. The inset shows the hysteresis loops for lower regions (± 500 Oe).

specimens were heated from room temperature to 1000°C at a rate of $10^\circ\text{C}/\text{min}$ in air. The TGA data reveals a sharp weight loss in the powder at 270°C because of the evaporation of water and organics [16]. This result is consistent with the DSC curve, which shows an exothermic peak at 280°C . An endothermic peak appears at 480°C and the powder weight (TGA curve) gradually increases and then stabilizes as the temperature exceeds 500°C . The main reason is that the CuO crystallization gradually forms with increasing temperature [17]. Based on these reasons, the CuO powder was annealed at 500°C to estimate the CuO crystallization.

Figure 2(a) shows the XRD patterns of as-grown CuO precursors and CuO powder annealed at 500°C for 1 h. Both samples were polycrystalline and had a monoclinic structure. An additional diffraction peak of $(\text{CH}_3\text{COO})_2\text{Cu}$ appeared in as-grown CuO precursors, indicating that a drying temperature of 120°C was insufficient for its evaporation. After thermal annealing at 500°C , the $\text{Cu}(\text{CH}_3\text{COO})_2$ phase

disappeared and the (111) diffraction peak dominated the CuO crystallization. The intensity of the major diffraction peaks increased, indicating that the sufficient thermal energy improved CuO crystallization. Based on the Scherrer formula [16], the grain size of CuO nanoparticles can be estimated from the full width at half-maximum (FWHM) of the (111) diffraction peak. The average grain size of CuO powder increased from 8 nm to 21 nm after thermal annealing at 500°C . This result is associated with the grains growing more easily under the higher temperature [16]. The ZnO powder was also synthesized and compared to $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powder. XRD analysis of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ ($x = 0, 0.33, 0.5, 0.67$, and 1) powders were conducted to analyze the effects of ZnO on $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ crystallization (Figure 2(b)). A small amount of ZnO mixing with CuO ($\text{Cu}_x\text{Zn}_{1-x}\text{O}$, $x = 0.67$), the monoclinic structure of CuO dominated the $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ crystallization, and ZnO phases existed in the $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ matrix. With increasing the ZnO concentration in $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ (x value increase from 0.67 to 0.33), the (101) diffraction peak of ZnO was the preferred orientation which indicated that the ZnO phases dominated the $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ crystallization. A comparison of the CuO revealed that the diffraction peak of (111) for $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ shifted to higher degree. In contrast, the diffraction peak of (101) for $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ shifted to lower degree comparing with ZnO. These results are associated with compressive strain in the crystallization [4]. In addition, the related (220) diffraction peak of the Cu_2O phase was attributed to insufficient oxidation [2]. Notably, the (200) diffraction peak of Cu_2O phase did not appear in $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ crystallization, indicating that the compositional ratio of Cu_2O phase was less than other $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.33$ and 0.67) powders. This result should affect the electrical properties of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders.

Figure 3 shows SEM images of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.33, 0.5$, and 0.67) powders at an annealing temperature of 500°C . All powders displayed a particle-like structure, and the agglomeration of particles was randomly distributed. The morphology of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder shows an irregular and its size for the agglomeration of particles is larger than that of $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ and $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ powders. The electrical properties of powder might be influenced by the particle size [18], therefore, the electrical resistance were examined.

Electrical measurements were conducted to determine the resistance value of CuO powder. The CuO powder was

FIGURE 5: XPS spectra of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder: (a) XPS spectrum of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder fully scanned from 300 eV to 1200 eV, (b) high-resolution selective spectrum of O, (c) high-resolution selective spectrum of Cu, and (d) high-resolution selective spectrum of Zn.

TABLE 1: The relation of electrical resistances and magnetic properties for $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ ($x = 0, 0.33, 0.5, 0.67$, and 1) powders with different CuO/ZnO ratios.

Sample			Resistivity ($\Omega/\square$)	Magnetism
$\text{Cu}_x\text{Zn}_{1-x}\text{O}$	Before annealing	$x = 1$	8.6×10^{11}	—
			2.3×10^6	AFM
	Annealed at 500°C	$x = 0.67$	1.0×10^7	DFM + PM
		$x = 0.5$	1.5×10^5	DFM + PM
		$x = 0.33$	8.2×10^8	DFM + PM
		$x = 0$	9.0×10^8	DM

pressed to form ingots (Φ 10 mm/ $\sim$ 2 mm thick) at a pressure of 30 kg/cm² for 30 s before measuring their resistivity (Table 1). After annealing at 500°C, the resistivity of the CuO sample decreased from $8.6 \times 10^{11} \Omega/\square$ to $2.3 \times 10^6 \Omega/\square$. After CuO mixing with ZnO, the electrical resistance of the $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ and $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ samples was higher than

that of CuO. This increment of the electrical resistance may be attributed to the substitution of Cu^+ ions at Zn^{2+} sites or the formation of electron trapping defect centers [19]. It is noted that the electrical resistance of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ sample ($1.5 \times 10^5 \Omega/\square$) decreased instead comparing with CuO sample. This result indicates that the ratio of the CuO phase to Cu_2O phase in $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ system decreased [20] and possessed a stable crystallization comparing with $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ and $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ samples.

To understand the contribution of CuO on the magnetic properties, the $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders with different ratios of CuO and ZnO were measured. Figure 4 shows the magnetization (M) as a function of magnetic field (H) at the temperature of 10 K for the $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders. All samples have a linear-like M - H variation at a magnetic field of ± 5000 Oe without measureable hysteresis, which indicates a paramagnetic behavior [21]. The magnetization of $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ sample was higher than that of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ and $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ samples, which indicated that the $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ powder contains a better paramagnetism (PM). The increment of antiferromagnetic interaction possibly reduced the PM that

resulted from the formation of CuO crystallization [21]. From XRD data (Figure 2(b)), the CuO phase dominated the $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$, $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ crystallization and affected their magnetic properties that were consistent with the result of M - H curves. In addition, the lower magnetization of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$, $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ was also attributed to the secondary phase of Cu_2O [22]. The low-field region of the hysteresis loops of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders was clearly observed (inset of Figure 4) which indicated that all $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders also contained a diluted ferromagnetism (DFM). The FM could be developed by the distortion of ZnO structure by the substitution of remnant Cu^{2+} ions into ZnO lattice [22, 23]. It is found that the coercivity field of the $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$, $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$, and $\text{Cu}_{0.67}\text{Zn}_{0.33}\text{O}$ powders is 75 Oe, 150 Oe, and 78 Oe, respectively. That is to say, the $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder has a good stability for thermal interference [24].

The chemical bonding of the $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder was examined by XPS with full region scanning from 0 eV to 1200 eV (Figure 5). In Figure 5(a), all peaks from oxygen, copper, zinc, and a trace of carbon are apparent, meaning that the $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder is substantially covered by Cu^{2+} , Zn^{2+} , and O^{2-} . The high-resolution scanning information provided in Figures 5(b)–5(d) is for the separate analysis of elements: O, Cu, and Zn, respectively. The high-resolution XPS spectrum of the O_{1s} signal (Figure 5(b)) indicates that the binding energy of 530.3 eV can be attributed to oxidized ions in the CuO particles [25]. Multippeak Gaussian fitting shows another O_{1s} peak located at 532.4 eV, indicating that this binding energy was dominated by Zn^{2+} ion doping [23]. The high-resolution XPS spectrum of the $\text{Cu}_{2p_{3/2}}$ mode (Figure 5(c)) appears at 932.3 eV, indicating the presence of Cu^{2+} ion [2]. The binding energy of 952.3 eV ($\text{Cu}_{2p_{1/2}}$ mode) can be attributed to Cu^+ ions in $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ that resulted from Cu_2O [26, 27]. This result is consistent with the observation of XRD data (Figure 3(b)). Figure 5(d) shows two strong peaks at 1021.5 eV and 1044.7 eV which correspond to $\text{Zn}_{2p_{3/2}}$ and $\text{Zn}_{2p_{1/2}}$, respectively. This is consistent with the Zn^{2+} ion binding in previous reports [28]. Based on these results, the Zn^{2+} ions were substituted by Cu^+ to form the Cu_2O phase that affects the electrical and magnetic properties.

The correlation of the magnetic properties and resistivity of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders were summarized in Table 1. The magnetic property of pure CuO powder varied from antiferromagnetism (AFM) to paramagnetism (PM) when ZnO to CuO. The resistivity of $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ powders decreased; the values of the paramagnetic behavior decreased. These results indicate that the paramagnetic behavior in $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ powder is the highest. The lower carrier concentration may promote paramagnetic ordering in $\text{Cu}_{0.33}\text{Zn}_{0.67}\text{O}$ [29].

4. Conclusions

The stability of oxide (CuO or Cu_2O) depends primarily on the intensity of oxidation (annealing temperature). When ZnO participated in the CuO system, the crystalline quality of CuO powder deteriorated. The ZnO mixing effect increased the crystallization size and induced a compressive stress in the particle. Although the presence of ZnO phases

deteriorated $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ crystallization, the electrical conductance was improved. A lower Cu_2O phase concentration and stable crystallization reduced the electrical resistance of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder. The electrical resistance of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{O}$ powder was the lowest and the magnetic behavior was the smallest because CuO and Cu_2O contents were higher. XPS analysis reveals that the Zn^{2+} ions were substituted by Cu^{2+} and Cu^+ ions, forming CuO and Cu_2O phases that confirmed the contribution of Cu_2O on the electrical and magnetic properties.

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