Synthesis of Zn$_{1-x}$Cu$_x$O Nanoparticles by Coprecipitation and Their Structure and Electrical Property

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Abstract. The Zn$_{1-x}$Cu$_x$O (x = 0 - 6% wt) nanoparticles has been synthesized by coprecipitation method using zinc acetate dihydrate, and copper powder were employed with HCl and NH$_4$OH respectively as solvent and precipitating agents. The effect of Cu concentration on structural, optical, and electrical properties of Zn$_{1-x}$Cu$_x$O nanoparticles were investigated. The diffraction patterns of XRD indicate that Zn$_{1-x}$Cu$_x$O phase crystallized in the wurtzite structure having crystal size which was evaluated by using MAUD software, in the range of 28 - 79 nm. Electron microscope analysis shows the morphology of Zn$_{1-x}$Cu$_x$O is nanowires, having finer grains with the increasing content of Cu. The Cu doping reduced the optical band gap energy from 3.10 eV to 2.80 eV, while the electrical conductivity increased from 1.18 x 10$^{-8}$ to 24.25 x 10$^{-8}$ S/cm. This result implies that Cu$^+$ or Cu$^{2+}$ ions have substituted Zn$^{2+}$ ions. However, doping of Cu more than 4% wt increase optical band gap which makes the electrical conductivity decrease. The electrical conductivity obtained from this study is significantly higher than that reported previously.

1. Introduction

Zinc oxide (ZnO) has emerged as a promising material for gas sensor, memory of optical and magnetic devices, piezoelectric transducers, photodiodes, photodetectors, UV-light emitting diodes (UV-LEDs), biomedical, solar cell, and transparent conductive oxide [1]. ZnO is a semiconductor oxide group II-VI with 3.37 eV direct band gap, large exciton binding energy of 60 meV exciton, high electron mobility at room temperature, high optical transparency and good in mechanical, magnetic, optical, and electrical properties. In addition, ZnO is also a metal oxide material that is inexpensive, nontoxic, resistant to radiation, and has a high thermal and chemical stability.

In the next generation, transparent conductive oxide (TCO) will involve the p-n junction, thus the fabrication of metal oxide semiconductor requires n-type and p-type TCO. However, the development of high-quality TCO thin film limited to increasing the n-type conductivity. While, fabrication of the p-type TCO thin films still complicated, thus it remains a major challenge until now [2]. The p-type TCO obtained by engineered the structure of ZnO with the addition of extrinsic doping with group IA and IB elements (Li, Na, K, Ag,Cu) in the place of Zn or by doping with group VA elements (N, P, As, Sb) in the place of oxygen to improve the electrical conductivity [3]. Among these doping elements, copper (Cu) is potential dopants to improve the electrical properties of ZnO, which has a low resistivity copper is (1.67x10$^{-6}$ Ω cm) [4]. The presence of copper (Cu) is used as a variable electrical conductance, thus it can control the electrical conductivity of ZnO. As a dopant element, copper has many physical and chemical properties that are similar to Zn, such as have the similar structure of the electron shells.
Synthesis of ZnO nanoparticles with addition of extrinsic doping can be done by using several methods such as auto-combustion, ball milling, sol-gel process, hydrothermal route, and co-precipitation method [4]. One of the promising inorganic compounds synthesis method is coprecipitation, which is based on precipitation of more than one compound simultaneously when passing through the saturation point. In this research, Zn_{1-x}Cu_{x}O (x = 0 – 6% wt) nanoparticles were synthesized by using coprecipitation method. The introduction of copper as dopant partially substituting Zn in ZnO powder and its effects will be studied in terms of structure, optical bandgap and electrical conductivity.

2. Experimental Procedure
The Zn_{1-x}Cu_{x}O (x = 0 – 6% wt) nanoparticles has been synthesized by coprecipitation method using zinc acetate dehydrate [Zn(CH_3COO)_2.2H_2O], and copper powder (Cu) as starting materials, which were mixed and dissolved in an appropriate amount of 0.5 M HCl using magnetic stirrer at speed of 350 rpm. The NH_4OH of 0.5 M was gradually added to the solution by titration method to achieve pH of around 9. The precursor solution stirred using a magnetic stirrer at 85°C for 4 hours. The precipitate formed from the process was then filtered and washed using distilled water, and dried in an oven at 100°C for 24 hours. The samples were then calcined in a furnace at 400°C for 3 hours.

The phase purity and crystal structure of samples were investigated by X-ray diffraction (XRD) using scanning angle 2θ ranging from 20°C to 70°C which operated at 40 kV and 30 mA with CuKα1 radiation at wavelength of 1.54 Å. The morphologies of Zn_{1-x}Cu_{x}O nanoparticles were studied using scanning electron microscopy (SEM). UV-Vis spectrophotometer was used to measure the coefficient of optical transmittance, thus through a calculation the value of optical band gap was obtained. The electrical conductivity of the samples were examined by LCR meter.

3. Result of Discussion

![Figure 1. XRD patterns of the Zn_{1-x}Cu_{x}O](image)

Fig.1 displays XRD patterns of Zn_{1-x}Cu_{x}O (x = 0 – 6% wt) nanoparticles calcined at 400°C for 3 hours. Diffraction peaks have been observed to be sharp which implies high crystallinity of Zn_{1-x}Cu_{x}O nanoparticles. The XRD data analyzed by software Match! was well matched with PDF (Powder Diffraction File) 00-079-0207 and has wurtzite crystal structure for all compositions. XRD results indicates that the Cu ions have substituted the position of Zn ions easily, due to the ionic radius of Cu⁺/Cu²⁺ closed to that of Zn²⁺. Theoretically, the copper with an atomic number of 29 has electron configurations that ends on d-orbital. Electron configuration of Cu is [Ar] 3d⁹ 4s¹ or [Ar] 3d¹⁰ 4s¹, so that both Cu⁺ and Cu²⁺ ions have a probability to present in the sample [2]. The presence of Cu⁺ ions in the ZnO lattice will contribute as an extrinsic dopant to form acceptor states in the energy band structure of ZnO, thus change an n-type of Zn_{1-x}Cu_{x}O to p-type semiconductor. Further, the presence of copper oxide phase has been detected at 5% and 6% wt Cu doped samples at diffraction angle (2θ) of 38.73°, though
the CuO peak are very small, it shows an impurity phase in samples. Lattice parameters analyzed by refinement method using software Rietica, particle size analyzed using software MAUD (Material Analysis Using Diffraction), and volume cell that obtained from the analyzed of XRD data are tabulated in Table 1.

| Copper content (% wt) | Crystallite size (nm) | Lattice Parameter | Volume Cell |
|-----------------------|-----------------------|-------------------|-------------|
| 0                     | 79                    | a = b (Å)         | c (Å)       | α = β (°) | γ (°) |           |
| 1                     | 65                    | 3.254066          | 5.211942    | 90       | 120   | 47.795048 |
| 2                     | 55                    | 3.250603          | 5.205092    | 90       | 120   | 47.630676 |
| 3                     | 50                    | 3.250454          | 5.205212    | 90       | 120   | 47.627419 |
| 4                     | 37                    | 3.250161          | 5.205280    | 90       | 120   | 47.619465 |
| 5                     | 30                    | 3.248422          | 5.202350    | 90       | 120   | 47.541725 |
| 6                     | 28                    | 3.248306          | 5.199845    | 90       | 120   | 47.515450 |

It can be seen in Table 1 that with the increasing content of copper, volume cell decreases for all samples. Lattice parameter decreases with the increasing copper content of the sample, due to replacing of Zn$^{2+}$ (0.73 Å) is smaller than that of Cu$^{2+}$ (0.74 Å). Surface morphologies of pure ZnO and Zn$_{0.97}$Cu$_{0.03}$O, which shown in Fig. 2, revealed the formation of nanowires and having finer grains for sample with the increasing content of Cu.

Figure 2. The morphologies of (a) pure ZnO, and (b) Zn$_{0.97}$Cu$_{0.03}$O nanoparticles

UV-vis spectrophotometer was used to analyze the optical band gap of the Zn$_{1-x}$Cu$_x$O as a semiconducting material. The transmission spectrum that has been obtained from measurements of UV-vis spectrophotometer was processed using Tauc Plot methods to obtain optical band gap. The Tauc relation to evaluate the optical band gap is shown on Eq. 1 [5].

$$(ahv)^{1/n} = A(hv - E_g)$$

where $A$ is a proportional constant, $E_g$ is the energy band gap of semiconductor material, $hv$ is the photon energy, and $\alpha$ is the optical absorption coefficient. The exponent $n$ depends on the type of electron transition of the material, because ZnO has a direct band gap, so $n = \frac{1}{2}$. The absorption coefficients were calculated by using Eq.2 :

$$\alpha = \frac{(-lnT)}{d}$$

where $T$ is transmittance of sample, and $d$ is width of the cuvette. Optical band gap of the Zn$_{1-x}$Cu$_x$O was obtained by plotting $(ahv)^{\frac{1}{2}}$ vs. $hv$ followed by extrapolating absorption edge by linear line in x-axis to find optical band gap [2].

The optical band gap energy and electrical conductivity of Zn$_{1-x}$Cu$_x$O nanoparticles are presented in Table 2. It is found that increasing of Cu concentration as dopant has reduced optical band gap energy from 3.10 eV to 2.80 eV, while the electrical conductivity increased from 1.18 x 10$^{-8}$ to 24.25 x 10$^{-8}$ S/cm. It implies that Cu$^+$ or Cu$^{2+}$ ions have substituted Zn$^{2+}$ ions side. However, at concentration of Cu doping more than 4wt%, optical band gap energy increase which lead to decreasing of electrical
This may possibly due to the heterogeneity of phase on the sample. Previous research carried out by Sonawane et al. (2008) [6] described that the Cu-doped ZnO nanoparticles prepared with the same method have much lower electrical conductivity in the range of $1.6 \times 10^{10}$ to $1 \times 10^{9}$ S/cm with monotonic increase in the increasing contain of Cu.

**Tabel 2.** The optical band gap energy and electrical conductivity of Zn$_{1-x}$Cu$_x$O nanoparticles

| Copper content (x) | Optical band gap energy | Electrical conductivity ($x 10^8$) |
|--------------------|-------------------------|-----------------------------------|
| 0 %wt              | 3.05 eV                 | 1.18 S/cm                         |
| 1 %wt              | 2.90 eV                 | 1.25 S/cm                         |
| 2 %wt              | 2.88 eV                 | 1.57 S/cm                         |
| 3 %wt              | 2.85 eV                 | 3.38 S/cm                         |
| 4 %wt              | 2.80 eV                 | 24.25 S/cm                        |
| 5 %wt              | 3.06 eV                 | 1.03 S/cm                         |
| 6 %wt              | 3.10 eV                 | 0.65 S/cm                         |

**Figure 3.** The optical band gap energy and electrical conductivity of Zn$_{1-x}$Cu$_x$O nanoparticles

### 4. Conclusion

The Zn$_{1-x}$Cu$_x$O nanoparticles has been successfully synthesized using coprecipitation method. Cu doping has led to the decreasing lattice parameters and forming finer grains of ZnO crystal. The presence of Cu until 4% wt has reduced the optical band gap energy, while the electrical conductivity increased by the presence of Cu$^+$ or Cu$^{2+}$ ions to create an acceptor energy level. For the whole samples, the significantly improved electrical properties have been obtained in this study compared to the previous report.

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