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The effect of Cu dopant on morphological, structural and optical properties of ZnO nanorods grown on indium tin oxide substrate

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Abstract. Zinc oxide (ZnO) is a promising semiconductor due to its tunable optical properties. Among semiconductor nanostructures, one-dimensional structure such as ZnO nanorods becomes the main focus due to their wide potential application. Cu doped ZnO has attracted much attention recently because of its interesting properties, such as room temperature ferromagnetism, multiferroics properties and green emission. In this work, we deposited ZnO nanorods on indium tin oxide coated glass substrates and then ZnO nanorods were grown and doped with three different Cu concentrations (1, 4 and 7 at. %) by hydrothermal method. The scanning electron microscope showed that ZnO nanorod were grown with a hexagonal shape with diverse growth orientation. The X-ray diffraction analysis reveals that the addition of Cu doping tends to increase the crystallite size and the lattice parameter. Generally, Cu doping reduces the absorbance at ultraviolet wavelength region except on the ZnO nanorods with 4% Cu. The addition of Cu also increases the bandgap energy and decreases the luminescence intensity in UV and visible regions, that is a sign that number of radiative transitions and the natural defects have been reduced.

1. Introduction

Zinc oxide (ZnO) is one of semiconductor materials that is intensively investigated by many researchers. Pure zinc oxide has a large band gap energy of 3.37 eV and large exciton binding energy of 60 meV at room temperature[1]. ZnO has significant potential for ultraviolet light detector, solar cells, and Light Emitting Diode (LED). Among the ZnO nanostructures, ZnO nanorods shows excellent properties due to bigger ratio area to volume ratios compare to other structures. Zinc oxide (ZnO) has grown by many methods, such as chemical bath deposition[2], spray pyrolysis[3] and hydrothermal deposition [4]. Recently, the properties of ZnO nanorods was successfully modified by the addition of metallic dopants. The addition of Cu element dopant is reported produce stronger luminescence in the blue region and ultraviolet [5], affects the orientation of crystal growth [6], enhances the photocatalytic activity[7], increases the dielectric constant [8] and even affects the ferromagnetic properties [9]. In this work, we synthesized Cu doped ZnO nanorods by ultrasonic spray pyrolysis and hydrothermal methods on the indium thin oxide (ITO) coated glass substrates. The main focus of this research is to study the effect of the Cu on the morphology, structural, and optical properties of ZnO nanorods.
2. Experimental
ZnO nanorods were grown on ITO coated glass substrates through two steps synthesis process. The first step is the deposition of ZnO seed layers using ultrasonic spray pyrolysis (USP) method and the second step is the growth of ZnO nanorods by using hydrothermal method. First, the seeding solution was made by dissolving 0.4 M zinc acetate dehydrate (\( \text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} \)) with deionized water. The solution was placed in the ultrasonic nebulizer container and then sprayed for 10 minutes onto the substrates heated at the temperature of 450°C. Second, the growth solution contains 0.1 M zinc nitrate tetrahydrate (\( \text{Zn(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \)), hexamethylenetetramine (\( \text{C}_6\text{H}_{12}\text{N}_6 \)), deionized water with three different copper (II) nitrate hemi(pentahydrate) (\( \text{Cu(NO}_3\text{)}_2 \cdot 2.5\text{H}_2\text{O} \)) concentrations (1, 4 and 7 at. %). The growth solution was stirred and heated at 60°C. The ZnO seed coated ITO substrates were then carefully immersed in growth solution and then heated at temperature of 95°C in the oven for 2 hours.

Morphological characterization was carried out using a Field emission scanning electron microscopy (FE-SEM) Inspert F50. From the SEM images, the diameter of ZnO nanorods was measured manually. The characterization of ZnO microstructure was performed using SHIMADZU XRD-7000 X-ray diffractometer. The optical properties characterization was conducted using Thermo Fisher Scientific GENESYS 10S UV Visible and FLS920 Fluorescence Spectrometer.

3. Results and discussion
Figure 1 shows the SEM images of ZnO nanorods doped with three different Cu concentrations. It was seen that the ZnO nanorods were grown with hexagonal shape. The undoped ZnO nanorods have random growth orientation and when Cu was added, the orientation of ZnO nanorods slightly changed to the direction of perpendicular to substrates surface. This result is similar with a previous work performed by Polat et al. [2]. The increasing of Cu concentration tends to reduce the diameter of nanorods from the approximately 128 nm into 83 nm. The decreasing of diameter ZnO nanorods may be due to the ion radius of Cu\(^{2+}\) ions (0.73 Å) that were substituted Zn\(^{2+}\) ions (0.74 Å) which have smaller ion radii[2]. The Cu dopant also tends to increase the density of the nanorods.

![Figure 1. SEM images of ZnO nanorods with Cu doping of (a)0, (b)1, (c) 4 and (d) 7 at.%](image-url)
Figure 2 shows the XRD pattern of ZnO nanorods with three different Cu concentrations. All ZnO nanorods samples show many diffraction peaks, indicating the ZnO nanorods were grown in random orientation, this agrees with the morphology as seen in figure 1. With the addition of Cu up to 7%, there are no new peaks found, it indicates that the Cu ions substitute the Zn ions and the role of Cu ions in ZnO structure as the deep acceptors bounding with oxygen ions [10].

![XRD pattern of ZnO nanorods doped Cu](image)

**Figure 2.** XRD pattern of ZnO nanorods doped Cu

Because of the intensity of (103) plane is dominant, hence (103) data are then processed to find the crystallite size, lattice parameters, density and volume crystal that all are summarized in table 1. The crystallite size was estimated from the Full Width Half Maximum (FWHM) data using the Debye-Scherrer formula [11]. Table 1 shows that generally the addition of Cu tends to decrease the crystallite size and we can confirm this result with the SEM results. The smallest crystallite size was achieved in ZnO nanorods doped with 4% Cu. With more Cu addition, we can see the increasing of crystallite size. This may be caused Cu ions did not only substitute the Zn ions but also filled the vacancy in ZnO lattice that made the structure get bigger. The density of ZnO nanorods also increased with the addition of Cu and this agrees with the SEM results. The lattice parameters also become smaller hence the volume of ZnO structure becomes smaller.

Figure 3 shows the absorption spectrum of Cu-doped ZnO nanorods. It is clearly seen that the absorption intensity at UV region is higher than the absorption at visible region, this transition is usually known as the absorption edge. This happened due to the wavelength at UV region has enough energy to excite the electrons to conduction band, while at the visible region, the energy is not enough for electron excitation hence the light will be transmitted or reflected. Figure 3 also shows that the addition of Cu doping concentration reduces the absorbance at ultraviolet wavelength region except the ZnO nanorods with 4% Cu that has the highest absorbance. Mittal et al [10] also reported the similar result where the addition of Cu tends to decrease the absorbance in UV region compared with undoped ZnO nanorods. The highest absorbance in ZnO nanorods with addition of 4 % Cu may be related to its morphology that has larger diameter and high density so it is more effective to absorb the ultraviolet light.
Table 1. Crystallite size, density, volume of Cu-doped ZnO nanorods

<table>
<thead>
<tr>
<th>Cu concentration (at. %)</th>
<th>Crystallite size (Å)</th>
<th>Density (g/cm³)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>alpha</th>
<th>beta</th>
<th>gamma</th>
<th>Volume (Å³)</th>
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<td>3.250</td>
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<td>90</td>
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<td>47.717</td>
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<td>3.247</td>
<td>5.209</td>
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<tr>
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<td>47.695</td>
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<td>5.200</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>47.584</td>
</tr>
</tbody>
</table>

Figure 3. Absorption spectrum of Cu-doped ZnO nanorods

Figure 4 shows the reflectance spectrum of Cu-doped ZnO nanorods. There is a sharp transition at a wavelength 370 nm – 390 nm corresponding to the absorption edge in figure 3. The addition of Cu in ZnO nanorods tends to decrease the reflectance in all wavelengths region.

The bandgap energy of ZnO nanorods was estimated from the reflectance data by using Kubelka-Munk formula and Taue-plot [11], [12] as shown in figure 5. The bandgap energy for ZnO nanorods with additions of Cu 0%, 1%, 4%, 7% are 3.095 eV, 3.121 eV, 3.123 eV, and 3.147 eV respectively. The addition of Cu increases the bandgap energy of ZnO nanorods linearly. This may occur due to Moss-Burstein effect, where the addition of Cu shifts the Fermi energy level in the bandgap[13].

Figure 6 shows the photoluminescence spectrum of Cu-doped ZnO nanorods. We can see that the luminescence of all samples have two emission peaks at wavelengths of 400 nm and 620 nm. The first peak is well known due to radiative transition from recombination of electrons with holes in the valence band [14]. The other peak at 620 nm is usually caused by the presence of intrinsic defects such as Zn vacancy, Zn interstitial, oxygen vacancy, oxygen interstitial or impurities [2]. The intensity of both peak decreased with Cu addition. Undoped ZnO nanorods have the highest luminescence, indicating the sample contains a lot of defects and the addition of Cu tends to decrease the luminescence intensity, that is a sign that defects have also been reduced. While we compare with
other works, Polat et al. [2], it has a different pattern where the addition of Cu tends to decrease the intensity in UV region and increase the intensity in the visible region.

**Figure 4.** Reflectance spectrum of Cu-doped ZnO nanorods

**Figure 5.** Tauc-plot of Cu-doped ZnO nanorods

**Figure 6.** Transmittance spectrum of Cu-doped ZnO

4. **Conclusion**

ZnO nanorods with three different Cu concentrations (1, 4 and 7 at. %) have been successfully synthesized through ultrasonic spray pyrolysis and hydrothermal methods. Based on the results of structural analysis, morphological and optical properties characterization, it can be concluded that the addition of Cu slightly changed the growth orientation of ZnO nanorods to the direction of perpendicular to substrates surface and the diameter of nanorods was reduced. The addition of Cu also tends to decrease the crystallite size and the lattice parameter. Generally, Cu doping reduces the absorbance at ultraviolet wavelength region except on the ZnO nanorods with 4% Cu. The addition of Cu also increases the bandgap energy and decreases the luminescence intensity in UV and visible regions that is a sign that the number of radiative transitions and the natural defects have been reduced.
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References
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D Annur, A Suhardi, M I Amal, M S Anwar, I Kartika.