The role of Mg dopant on the morphological, structural and optical properties of Mg doped zinc oxide grown through hydrothermal method

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Abstract. ZnO nanorods is a low cost II-VI semiconductor compound with huge potential to be applied in optoelectronic devices i.e. light emitting diodes, solar cells, gas sensor, spintronic devices and lasers. In order to improve the electrical and optical properties, group II, III and IV elements were widely investigated as dopand elements on ZnO. In this work, magnesium (Mg) was doped into ZnO nanorods. Samples were prepared firstly by deposition of undoped ZnO seed layer on indium thin oxide coated glass substrates by ultrasonic spray pyrolysis method and then followed by the growth of ZnO nanorods doped by three different Mg concentrations by hydrothermal method. Based on the morphological, microstructural and optical characterizations results, it is concluded that the increase of magnesium concentration tends to reduce the diameter of ZnO nanorods, increases the bandgap energy and decreases the UV absorption the luminescence in UV and visible range.

1. Introduction

In recent years, the properties of nanomaterial have been widely investigated by the scientists. Among semiconductor nanostructure, ZnO nanorods have attracted many scientists and engineers because of its wide application in optoelectronics, sensor and actuator, energy and biomedical [1]. ZnO is a low cost and eco-friendly II-VI semiconductors which is easily synthesized. ZnO has many advantages among those semiconductors, such as it can be grown at low temperature (<500°C) [2], wide direct band-gap energy (3.37 eV) [3] and large exciton binding energy (60 meV) [4].

Various methods have been introduced for the preparation of ZnO nanorods, such as vapour liquid solution deposition, pulsed laser deposition, spray pyrolysis and metal organic chemical vapour deposition (MOCVD) [2]. Each of these methods has their own advantages and disadvantages. Hydrothermal method is a preparation method which is simple, low cost and can be performed at low temperature without high vacuum condition [2].

Many researchers reported the properties of ZnO nanorods can be modified by the addition of doping elements. In 2009, Te Hua Fang et al showed that the magnesium addition into ZnO nanorods was able to increase the electrical conductivity [5], improved the optoelectrical properties in the ultraviolet detector [6] and also could increase the selectivity when it was applied as ethanol sensor [7].

This work reports the effect of three different concentrations of magnesium (0, 1 and 7 at. %) on the morphological, microstructural and optical properties of ZnO nanorods. Samples were grown on...
indium thin oxide coated glass substrates through deposition of a seed layer by ultrasonic spray pyrolysis method, and then followed by growth of ZnO nanorods by hydrothermal method.

2. Experimental
ZnO nanorods were synthesized through two steps. The first step was the deposition of seeding layers on the ITO substrates using ultrasonic spray pyrolysis method. The seed solution consisted of 0.2 M zinc acetate dehydrate ((CH₃COO)₂Zn.2H₂O) dissolved in the deionized water. The solution was stirred at 400 rpm at room temperature, and then put into a container inside the commercial ultrasonic nebulizer, while a clean coated ITO glass substrate was put on a hotplate at the temperature of 550°C. The droplets of seed solution were then sprayed onto the substrates surface using the ultrasonic wave (1.7 MHz) for 10 minutes. The next step was the growth process of Mg-doped nanorod ZnO using hydrothermal method with three variation of magnesium concentrations (0, 1 and 7 at. %). The growth solution contained of 0.2 M zinc nitrate tetrahydrate (Zn(NO₃)₂.4H₂O), hexamethylenetetramine (C₆H₁₂N₄) and magnesium nitrate hexahydrate (Mg(NO₃)₂ that were dissolved in the deionized water and stirred at 400 rpm until its temperature reached 60°C. The growth process was started by put the substrates into the growth solution and heated at 95°C in oven for 2 hours.

Morphological characterization was carried out using a field emission scanning electron microscopy (FE-SEM) Inspect F50, microstructural properties were investigated by Shimadzu XRD-7000 X-Ray Diffractometer and the optical properties were characterized by Thermo Fisher Scientific GENESYS 10S Ultraviolet Visible, Hitachi UV-Vis Spectrometer U-3900H and FLS920 Fluorescence Spectrometer.

3. Result and discussion

3.1. Morphological properties
Surface morphology of the ZnO nanorods is shown in figure 1. Generally, ZnO nanorods were growing overlap with each other. The growth direction of ZnO nanorods was not uniform and not too perpendicular to the ITO substrates compared to other previous results [8]. From this figure, it can be seen that the increase of magnesium concentration tends to reduce the diameter of ZnO nanorods. This may occur as a result of the substitution of Mg into ZnO with an ionic radius which was smaller than Zn ions. This result is different with the previous other result showing that the addition of Mg doping resulted in an increase of diameter of ZnO nanorods [5].
Figure 1. SEM images of Mg doped ZnO nanorods with a concentration of (a) 0%, (b) 1% and (c) 7 at. %

3.2. Microstructural properties
The XRD diffraction pattern of ZnO nanorods is shown in figure 2. The diffraction pattern shows the peaks of ZnO phase with the crystal planes of (100), (002), (102), (101), (110) and (103), while the other peaks come from the indium tin oxide substrate. In general, position of the peaks is same for three different samples. It indicates that the addition of Mg doping does not produce the other materials phase because Mg$^{2+}$ ions were able to be completely substituted to the Zn$^{2+}$ ions or as an interstitial site in the ZnO crystal [9].

The diffraction pattern which has many peaks also indicates that the direction of crystal growth of ZnO nanorod is not uniform. Furthermore, it can be observed that the addition of Mg dopant results in the decrease of peak intensities of (002), (102) and (103) crystal planes. This result has a close agreement with the SEM results that there is no any dominant growth directions of ZnO nanorods.
3.3. Optical properties

3.3.1. Absorbance and transmittance spectra. Figure 3 shows the absorbance and transmittance spectrum of ZnO nanorods. The absorbance spectra show that the intensity at a wavelength of 380 nm which is known as the absorption edge that correlated with band gap energy is sharply decreased. The addition of Mg dopant decreases significantly the absorption intensity in the ultraviolet region (300-380 nm). In the visible region, the addition of 1 at.% Mg leads to increase the absorbance intensity while the addition of 7 at.% Mg leads to decrease the absorbance intensity. The decrease of absorbance values in UV region could be related to the smaller diameter of nanorods that less effective for UV light absorption.

Figure 2. X-ray diffraction pattern of the Mg-doped ZnO nanorods

Figure 3. Absorbance spectra of Mg doped ZnO nanorods
3.3.2. Reflectance spectra and Tauc Plot graph. Figure 4(a) is the reflectance spectra of ZnO nanorods. This figure shows that for all samples, the reflectance intensity increases significantly at a wavelength of 380 nm. It is corresponding to the absorption edge as shown in Figure 3. The bandgap energy calculation of ZnO nanorods was performed based on the diffuse reflectance spectra by using Kubelka Munk equations[9]. The calculated data were then interpolated in Tauc plot as shown in figure 4(b). The result shows that the bandgap energy for undoped ZnO nanorods is 3.11 eV while the ZnO nanorods with Mg concentrations of 1 and 7 at. % are 3.18 eV and 3.15 eV, respectively. The increase of bandgap may occur due to the Moss-Burstein effects, namely the shifting of the Fermi energy to the conduction band due to the high concentration of dopant elements so that the energy gap becomes wider [10].

![Figure 4](image)

**Figure 4.** (a) Reflectance spectra and (b) Tauc Plot of Mg doped ZnO nanorods

3.4. Photoluminescence spectra

Figure 5 shows the photoluminescence spectra of ZnO nanorods. In this figure, it appears there are two peaks at the wavelengths of 400 nm and 630 nm. The luminescence intensity at lower wavelength represents the radiative transition from the recombination of the conduction band electrons with the valence band holes. The luminescence at a wavelength of 630 nm may occur due to many natural defects in ZnO nanorods. The increase of Mg concentration in ZnO nanorods appears to decrease the luminescence in the entire wavelength range.
4. Conclusion
In this study, ZnO nanorods have been successfully synthesized with the ultrasonic spray pyrolysis and hydrothermal method. ZnO nanorods are mostly growing overlap with no uniformity and not exactly perpendicular to the substrate in the growth direction. The increase of magnesium concentration tends to reduce the diameter of ZnO nanorods and decreases the intensity of almost all diffraction peaks of ZnO rods. The addition of Mg dopant of one and 7 at. % is found to decrease significantly the absorption intensity in the ultraviolet region (300-380 nm) and increases the bandgap energy from 3.11 eV into 3.18 eV and 3.15 eV, respectively. The photoluminescence spectra show there are two peaks at the wavelengths of 400 nm and 630 nm that represent the radiative transition from the recombination of electrons and holes and the presence of the natural defects in ZnO nanorods, respectively. The increase of Mg concentration in ZnO nanorods appears to decrease the luminescence in the UV and visible range.

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