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Effects of Mn Dope on Morphological, Structural and Optical Properties of ZnO Nanorods Grown by a Hydrothermal Method

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Abstract. ZnO nanorods were grown on glass substrate has been systematically investigated by varying Mn doping concentrations. The nanorods have been developed by a simple hydrothermal method on the ZnO seed layer which were deposited by ultrasonic spray pyrolysis method. The influences of Mn on the morphological, structural and optical behavior were observed by measuring Scanning Electron Microscope, X-Ray Diffraction, and UV-Vis spectrophotometer, respectively. It is found that the nanorods growth without any orientation. Interestingly, all the nanorods under investigated exhibit a polycrystalline hexagonal wurtzite structure with strong absorption in UV region and a high transparency in the visible region suggesting that optical properties of ZnO nanorods have been modified by Mn doping.

INTRODUCTION

Diluted Magnetic Semiconductors (DMSs) are formed by partial replacement of the cations of nonmagnetic semiconductors by magnetic transition-metal (TM) ions [1]. In this case, the doped wide bandgap semiconductors in which transition-metal ions substitute cations sites tend to be ferromagnetic at room temperature. DMSs oxide such as ZnO, TiO₂, and SnO₂ offers a wide range of applications such as optical and spintronic devices [2–5].

Zinc Oxide (ZnO) is a hexagonal wurtzite structure semiconductor that has a wide band gap (Eg = 3.37 eV) and exciton binding energy (60 meV) [5, 6]. ZnO is also strong room temperature luminescence, high transparency, and high electron mobility [5]. ZnO is a safe host material that can be doped with different metal ions. Doping of transition metal ions such as Mn, Co, Ni into ZnO can change the band gap, the crystallite size and other properties [5]. Nowadays, Mn is a potential candidate as a dopant to realize DMS based ZnO. Furthermore, by additional Mn concentration into ZnO, some properties will be observed, such as strong visible emission at room temperature [5] and increasing band gap [7].

Mn-doped ZnO had been successfully prepared by different methods such as hydrothermal [1,2], co-precipitation [3], wet-chemical method [4], sol-gel [6] and spray pyrolysis [7, 8]. Among these methods, ultrasonic spray pyrolysis (USP) and hydrothermal method have been chosen because it offers several advantages such as simplicity and low cost.

In this work, we have synthesized Mn-doped ZnO nanorods by hydrothermal method with different doping concentration (0%, 3%, and 7%) on a glass substrate at low temperature (95°C). Then, the detail studies of structural, morphological and optical properties of Mn-doped ZnO nanorods are discussed systematically.

EXPERIMENTAL

In this experiment, undoped ZnO and Mn-doped ZnO nanorods with different Mn concentration (3 wt.% and 7 wt.%) were grown on a glass substrate with two different methods. ZnO seed layers were deposited by USP method
and the growth of ZnO nanorods were formed by a hydrothermal method. For the seed layers, 0.2 M zinc acetate dehydrate \((\text{C}_2\text{H}_3\text{O}_2\text{Zn}.2\text{H}_2\text{O})\) was dissolved in de-ionized (DI) water at room temperature. The solution was placed into the nebulizer and then sprayed for 12 minutes. The glass substrates were kept at 480°C during deposition. For the growth, 0.05 M zinc nitrate tetrahydrate \((\text{NH}_4\text{O}_2\text{Zn}.4\text{H}_2\text{O})\) and hexamethylenetetramine \((\text{C}_6\text{H}_{12}\text{N}_2)\) were dissolved in DI-water. The dopant source of manganese was manganese chloride tetrahydrate \((\text{MnCl}_2.4\text{H}_2\text{O})\). Manganese chloride tetrahydrate mixed into zinc nitrate tetrahydrate and hexamethylenetetramine solution at room temperature. Then, the substrates were immersed and heated at temperature 95°C in an oven for 1.5 hours.

The crystallite structure of the samples was characterized by X-ray Diffraction (XRD) by using Rigaku Smartlab 3kV. The morphological and optical properties of Mn-doped ZnO were determined by using Scanning Electron Microscope (Hitachi SU3500) and the optical properties were determined by using Genesys 10S UV-Vis spectrophotometer in the range of 250-700 nm.

RESULTS AND DISCUSSION

The morphology of Mn-doped ZnO nanorods was investigated by SEM. As shown in Fig.1, the undoped and Mn-doped ZnO nanorods have been grown with random alignment. Even though, some areas covered with impurities. There are gaps between every rod at the undoped ZnO. Furthermore, by additional Mn 3 wt.% the rods are smaller and denser. Meanwhile, for Mn 7 wt.% the impurities have almost covered up the surface area, but we can see that the density of nanorods is less than Mn 3 wt.%.

The XRD patterns of undoped and Mn-doped ZnO nanorods are shown in Fig. 2. All samples show a polycrystalline hexagonal wurtzite structure and there is no other secondary phase was detected in the XRD patterns. The strong and sharp peaks indicated that the samples of Mn 3 wt.% doped ZnO are polycrystalline. ZnO undoped have a strong diffraction peak at (002) shows that the crystal orientation of undoped ZnO nanorods is along z axis. Three dominant diffraction peaks have determined for Mn-doped ZnO (3% and 7%) nanorods, (001), (002) and (101) indicate that ZnO nanorods were grown in a random alignment. The calculated lattice parameters of Mn-doped ZnO is higher than the undoped ZnO nanorods (Table 1), because the Zn\(^{2+}\) ions with a small ionic radius (0.74 Å) are replaced by Mn\(^{2+}\) ions with a large ionic radius (0.83 Å) [9, 10].

Analysis of optical properties was determined using UV-Vis spectra. Figure 3 shows the UV-Vis absorption spectra of undoped and Mn-doped ZnO nanorods, which exhibit a strong absorption in UV region and a high transparency at the visible region. The highest absorbance peak is Mn 3%, it may be caused by the dimension of nanorods compared to the other Mn concentrations. Furthermore, the highest absorbance indicated that the number of energy level due to defect is lower. The shortest peak is Mn 7%, the impurities that covered up the surface may cause the sample cannot absorb the incident light properly instead of the existence of defects which originate from deep level emission.

![Figure 1](image1.png)

**FIGURE 1.** SEM images of (a) Mn 0% (b) Mn 3% (c) Mn 7% doped ZnO nanorods.
FIGURE 2. X-ray diffraction patterns of undoped and Mn-doped ZnO nanorods.

FIGURE 3. Effect of Mn dope concentration on UV-Vis absorbance spectra of ZnO nanorods

<table>
<thead>
<tr>
<th>Doping Concentration</th>
<th>Crystalline Size (Å)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
</tr>
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<tbody>
<tr>
<td>Mn 0 %</td>
<td>395.6</td>
<td>3.25056</td>
<td>3.25056</td>
<td>5.20601</td>
<td>47.63787</td>
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<tr>
<td>Mn 3 %</td>
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<td>3.25197</td>
<td>5.20880</td>
<td>47.70464</td>
</tr>
<tr>
<td>Mn 7 %</td>
<td>394.1</td>
<td>3.25248</td>
<td>3.25248</td>
<td>5.20865</td>
<td>47.71832</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Undoped ZnO and Mn-doped ZnO nanorods have been synthesized by a simple hydrothermal method. The SEM images show that the ZnO nanorods had random alignment with smaller diameter provide by Mn doped ZnO (3 wt.%). The XRD spectra confirm that the Mn doped ZnO nanorods have a polycrystalline structure, while, the Mn 3 wt.% doped ZnO has strong peaks at (001), (002), and (101). The UV-Vis spectra showed that the optical properties of undoped and Mn doped ZnO had different absorption and transmission level. The Mn doped ZnO (3 wt.%) has strong absorption in the range of UV and visible, while, the transmission spectra of Mn doped ZnO (3 wt.%) show lower intensities.
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