Effect of pH on the Crystal Growth of ZnO Nanomaterials and Their Band gap Energies

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Abstract. Zinc oxide nanostructures with vary pH have been successfully synthesized using a sol-gel method. The nanostructured materials were annealed at low temperature of 300 °C for 3 hour. The effect of pH of the synthesis condition of ZnO on the structural and optical properties of the nanostructures were studied using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-Vis spectrophotometer. XRD results revealed that only sample at very acidic condition was not pure with the presence of impurities. This implies that acidic condition require more energy in order to produce pure and single phase of ZnO nanostructures. FESEM results showed that at very acidic and basic condition, the crystallites tended to agglomerate to form bigger particles. The band gap energy of the ZnO nanostructures at pH 6 and 9 were 3.276 and 3.300 eV respectively. Interestingly, it was found that as the aspect ratio of nanorods increased, the band gap energy of the material also increased.

1. Introduction

Zinc oxide (ZnO) has received much attention from many researchers as promising candidate for semiconductor device applications [1-4]. This is due to their properties of wide and direct band gap semiconductor (3.37 eV) at room temperature [3, 5-9]. ZnO is being considered as a strong competitor to GaN, which also possess hexagonal structure but the advantage of ZnO over GaN is that ZnO has a large exciton binding energy (60 meV) that should favour light emission at room temperature. Therefore, ZnO has applications in ultraviolet (UV) optoelectronic devices such as UV light detectors, UV light emitting diodes, p-n junction devices and semiconductor lasers. ZnO also has been used in piezoelectronic transducers, gas sensors, transparent conductive films and bulk acoustic wave devices [5].

A wide variety of techniques have been used to synthesize ZnO nanostructures. This includes the hydrothermal methods [4], pulsed laser deposition (PLD) [5], combustion [10], and sol-gel method.
1. Different synthesis method will yield different type of morphology. ZnO is famous for having variety of morphology such as rod, spherical, needle, tube, flower and etc [2, 11]. Each morphology will have different properties that will suit a particular applications. So, it is very important to be able to control the synthesis route in order to obtain desired morphology. This work has focused on the effects of pH condition on the structural, morphology and also the optical properties of ZnO.

2. Experimental
The synthesis of ZnO nano powders were prepared by using a sol-gel method. The starting materials used was zinc acetate dehydrate (R & M chemicals, 99.5% purity). This material as first has been dissolved with absolute ethanol and then was stirred for about 1 hour. The pH of the material was adjusted to acidic condition using 1.0 M of nitric acid. Whereas for basic condition, the solution was added with 1.0 M of ammonium hydroxide. In this work, 3 different pH condition were studied which were pH 3, 6 and 9. After the desired pH of the solution was obtained, the material was slow dried and a white precursor was obtained. The samples were then ground using an agate mortar to obtain fine powders of ZnO. Thermal studies were done by using a simultaneous thermogravimetric analyzer (STA), SETARAM SETSYS Evolution 175. Based on the TG/DSC, the precursors were annealed at 300 °C for 3 h. The annealed precursors were characterized by using X-ray diffraction (XRD) using the PANalytical X’pert Pro MPD diffractometer. The morphology and crystallite size of the materials were then examined by using field emission scanning electron microscopy (FESEM - JEOL JSM-7600F). The band gap energies of the materials were determined using a UV-Vis spectrophotometer, the Perkin Elmer Lambda 950 UV-Vis-NIR. The measurements were done in reflection mode and in ambient conditions.

3. Results and discussion
The XRD patterns for ZnO nanostructures annealed at 300 °C for 3 h are shown in Fig. 1. The diffraction patterns show that only ZnO pH 6 and 9 sample were in good agreement with the ICDD reference number 01-089-0511 indicating that the synthesized samples were single phase with hexagonal structure and space group P63mc. Whereas for ZnO pH 3 sample was impure due to the acidic condition (pH 3) consist of high concentration of H⁺ ion that leads to the difficulty for precursor to form ZnO and more energy are needed in order to form pure ZnO phase. For the pH of 6 and 9, and due to the low concentration of H⁺ and high concentration of OH⁻, the formation of ZnO are much easier compared to pH 3 condition. The reaction between OH⁻ and Zn⁺ plays an important role in the formation of ZnO nanostructures [12]. The narrow and high intensity peaks for pure samples showed that the synthesized ZnO samples were well crystalline.
Figure 1: The XRD patterns of (a) ZnO ICDD 01-089-0511 (b) pH 3 (c) pH 6 and (d) pH 9 of ZnO annealed at 300 °C for 3 hour.

FESEM images of ZnO with varies pH are shown in Fig. 2. It can be seen that for impure ZnO pH 3 sample (Fig. 2 (a)) has cube like shape. Meanwhile, the morphology for pure ZnO pH 6 and 9 samples were short and long nano rods shape. It was found that the sample synthesize at very acidic medium cause the crystallites to become agglomerate and form bigger particles. For sample that
synthesize at basic medium shown in Fig. 2 (c), it was found that the sample possess very long and thin nano rods shape. These long and thin nano rods were stick together to form bigger rods. Unlike at very acidic and basic medium, for pH 6 it can be seen clearly that the crystallites were not agglomerate. The average dimension and aspect ratio for pure samples were obtained by measuring the dimension of 50 crystallites for each sample and listed in Table 1.

![Figure 2: The SEM images of (a) pH 3 (b) pH 6 and (c) pH 9 of ZnO annealed at 300 °C for 3 hour.](image)

| Sample  | Morphology     | Diameter (nm) | Length (nm) | Aspect ratio (Length/Diameter) |
|---------|----------------|---------------|-------------|--------------------------------|
| ZnO_pH 6 | Short rods     | 82.50         | 899.15      | 10.90                          |
| ZnO_pH 9 | Long nanorods  | 73.62         | 1652.39     | 22.44                          |

Further studies on the light absorption properties of pure samples have been carried out using UV-Vis spectrophotometer. Fig. 3 (a) shows the UV-Vis reflectance curves of ZnO nano rods. The nano rods sample were measured at room temperature in the wavelength of 200-800 nm. It was found that the absorption edge of the ZnO pH 9 was slightly shifted to the left as compared to ZnO pH 6 sample. This indicates that the absorption wavelengths have decreased. Band gaps can be evaluated from the absorption edges. The band gap energies of ZnO materials were determined by using Tauc plots. Equation (1) below is used,

\[(\alpha \nu h)^2 = C' (h \nu - E_g)\]  

where \(\alpha\) is the absorption coefficient of the ZnO at a certain value of wavelength \(\lambda\), \(h\) is Planck's constant, \(C'\) is the constant, \(\nu\) is the frequency of light, \(E_g\) is the band gap energy. The Tauc plot graph for ZnO pH 6 and 9 samples are shown in Fig. 3 (b). The determination of band gap energy using Tauc plot graph was explained by R. Rusdi et al. [2]. The band gap energy for ZnO pH 6 and 9 are 3.276 and 3.300 eV respectively. It was found that nano rods with higher aspect ratio have larger band gap energy. The dimension of the crystallites plays critical role in the band gap energy of the materials. The effects of dimension of crystallites on the band gap energy of materials were well studied in our previous work [1].
4. Conclusion

The ZnO with morphology of long nano rods have successfully synthesized via sol-gel method at very low temperature. It was found that basic synthesis condition was more easy and suitable to obtain ZnO nano rods compared to acidic condition. The morphology of the materials with vary pH revealed that pH affected the shape of the crystals. The very acidic and basic ZnO nanostructures tended to form agglomeration and then leaded to bigger particles. At very basic condition, it was found that ZnO had very long rods which were 1652.39 nm. It was also found that the ZnO nano rods with higher aspect ratio had larger band gap energy. In conclusion, by controlling the pH, the desired morphology of the crystals can be obtained.

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