Proceedings of the 2nd International Congress APMAS2012, April 26–29, 2012, Antalya, Turkey

# Effects of pH Value on the Growth and Structural Properties of Sol–Gel Synthesized Nanostructured ZnO

D. Gültekin*, M. Alaf and H. Akbulut
Sakarya University, Engineering Faculty, Metallurgical & Materials Engineering Department
Esentepe Campus, 54187, Sakarya, Turkey

The aim of the research presented is to investigate the effect of pH value on the structural and morphological properties of nanostructured ZnO products. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) has been used as precursor whereas distilled water is used as a solvent. The pH value of the sol was adjusted with monoethanolamine (MEA) and it changed from acid to base in nature. X-ray diffractometer has been used to determine preferred crystal orientation and particle size of the thin films. Film morphologies have been examined by using JEOL JSM 6060 LV scanning electron microscope equipped with energy-dispersive spectroscopy.

DOI: 10.12693/APhysPolA.123.330
PACS: 61.46.Df, 81.07.Wx, 81.20.Fw

## 1. Introduction

Zinc oxide (ZnO), a semiconductor with a direct wide band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV) [1, 2], is one of the most promising materials for applications in catalysts, sensors, piezoelectric transducers, transparent conductors, and surface acoustic wave devices [2]. With this unique property, ZnO has also attracted attention for electrical and optical applications such as light-emitting diodes, photocatalysts, photodetectors, solar cells, piezoelectronic devices, and sensors. Because the shape of the ZnO particles depends on the reaction conditions during their formation, many methods have been used to synthesize ZnO particles [1]. In addition to the conventional solid-state process, many other synthetic routes, such as hydrolysis, pyrolysis, hydrothermal methods and precipitation have been introduced to prepare nano or microscaled ZnO particles in various sizes and morphologies over the past few years [3].

The precipitation of ZnO particles has been usually described through a growth unit that might be either $Zn(OH)_2$ or $Zn(OH)_4^{2-}$ ions depending on the pH, temperature and synthetic methods [1]. Sagar et al. [4] examined the role of pH value on the structural properties of ZnO films and investigated the basic nature of the modified sol as a function of increase in the ratio of additive MEA to zinc acetate dihydrate (ZnAc) precursor. The pH of modified sols was found to increase continuously from 6.4 to 10.6 with increase in value of MEA. The increase in pH with addition of MEA clearly indicates an increase of alkaline nature of the prepared sols. This increase is attributed to hydrolysis of salts of weak acid in strong base medium. The higher alkaline nature of sols is reported to be useful in enhancing the formation of ZnO crystallites.

*corresponding author

## 2. Experimental

Figure 1 represents the process flow chart used for synthesis of nanostructured ZnO powders by homogeneous precipitation. ZnAc ($Zn(CH_3COO)_2{\cdot}2H_2O$) was used as a precursor whereas distilled water as a solvent. Monoethanolamine (Merck) was used for adjusting of sol pH. MEA was added to homogeneous and transparent solution until white precipitates are obtained. After the precipitation, collected nanosized powders were dried at 100 °C and annealed at 400 °C. X-ray diffractometer (Rigaku D/MAX 2000) has been used to characterization of coatings. Film morphologies have been examined by using scanning electron microscope (SEM) (JEOL JSM 6060 LV).

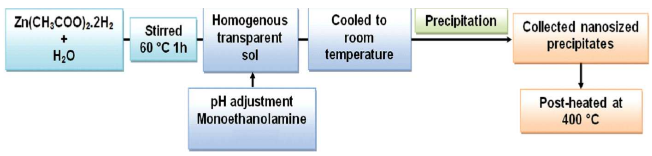


Fig. 1. Flow chart for synthesis of nanostructured ZnO powders by homogeneous precipitation.

## 3. Results

Figure 2 shows the XRD patterns of ZnO powders as a function of pH value. The peak positions in each product agree well with the reflections of bulk ZnO (JCPDS 01-076-0704). As could be seen from the XRD patterns, all products have polycrystalline nature. From the as-prepared ZnO no secondary phase other than ZnO was observed in the XRD patterns. ZnO powders show a highly oriented (101) peak and (100) and (002) peaks. There have been significant changes in orientation and the peak intensities with the increase in pH values. The addition of MEA changes the alkaline nature of the prepared sols that give ZnO films with improved crystalline quality. The improvement in microstructural and optical properties may be attributed to strong alkaline nature of the sols as the MEA in the sol improves the stability and homogeneity of the sol by preventing uncontrolled hydrolysis [5].

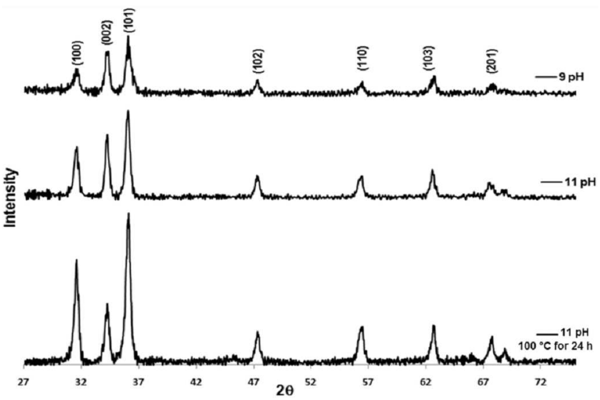


Fig. 2. XRD results of nanostructured ZnO products.

The formation of ZnO particles from the hydrolysis of $Zn^{2+}$ ions in aqueous media is known to be a complex process. Many polyvalent cationic species can be formed between $Zn_{2+}$ ions with $OH^-$ ions and are strongly dependent upon the pH of the solution. However, the precipitation of ZnO particles has been usually described through a growth unit that might be either $Zn(OH)_2$ or $Zn(OH)_4^{2-}$ ions depending on the pH, temperature, and synthetic methods [1]. The formation of ZnO by hydrolysis and condensation of the dissolved species taking into account the participation of $CH_3COO^-$ ions as good complexant for $Zn^{2+}$ ions [6].

The higher alkaline nature of sols is reported to be useful in enhancing the formation of ZnO crystallites. In our study, MEA was added to homogeneous and transparent Zn-sol until white precipitates are obtained. The pH values were recorded as 9 and 11. The addition of MEA changes the alkaline nature of the prepared sols that give ZnO films with improved crystalline quality. The improvement in microstructural and optical properties may be attributed to strong alkaline nature of the sols as the MEA in the sol improves the stability and homogeneity of the sol by preventing uncontrolled hydrolysis [4].

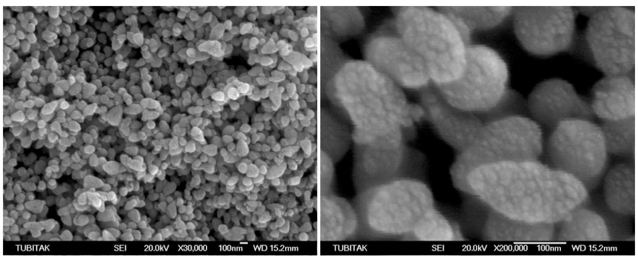

Fig. 3. FESEM images of ZnO nanostructure powders produced at pH 9.

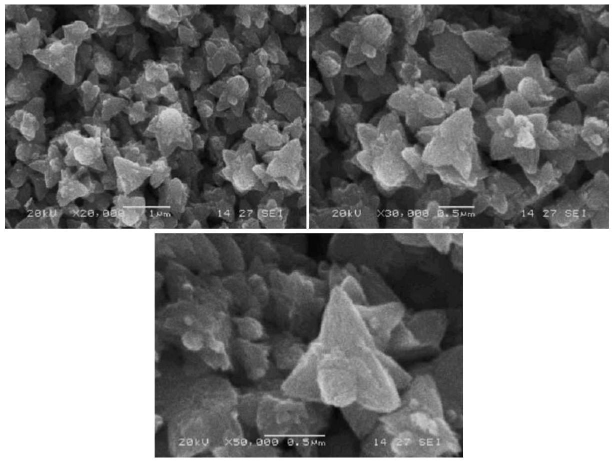

Fig. 4. SEM images of ZnO prism-like nanoflowers powders produced at pH 11.

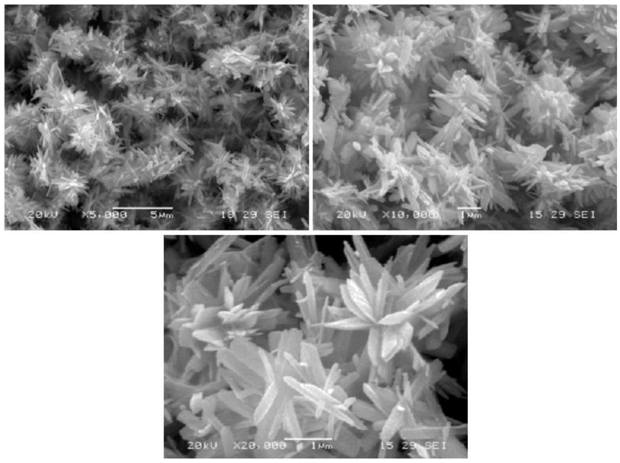

Fig. 5. SEM images of nanorods like ZnO produced at pH 11 — holding at 100 °C for 24 h.

FESEM/SEM images of synthesized ZnO nanopowders have been shown in Figs. 3, 4, and 5. Literature data [3, 4] shows that additives (i.e MEA, NaOH) and pH play an important role in solution that they have a strong effect on the formation of ZnO different nanostructures such as nanorods, nanoflowers, etc. In Fig. 3, the ZnO powders exhibit a porous spherical nanostructure with the particle sizes approximately between 28 and 30 nm which were calculated with Scherrer's formula. In the literature, ZnO nanostructures having 9–250 nm have been reported [5, 7]. As can be seen from the FESEM image of ZnO in Fig. 3, the nanostructure has approximately 0.1 $\mu$m sized nodules which consist of agglomerated ultrafine particles. These ultrananograins have agglomerated and have formed large grains after the heat treatment. When pH level increases to 11, prism-like nanoflowers structure was observed (Fig. 4). Some amount of the precipitates were held in a furnace for 24 h at 100 °C and after they were heat-treated at 400 °C, whose SEM images represent in Fig. 5 that ZnO nanostructures look like nanorods.

## 4. Conclusions

Polycrystalline and nanostructured ZnO powders were successfully produced by homogeneous precipitation route. The effects of pH on the structural and crystalline properties have been presented. Experimental results showed that the crystal orientations and crystalline structures were affected with pH. Each of products have nanostructured particles which shape nanoparticles, nanoflowers, nanorods and hexagons. As could be seen from the XRD patterns, all films have polycrystalline nature. The intensity of the peaks and the orientation were predominantly determined by pH value.

## Acknowledgments

The authors would like to acknowledge the financial support of Sakarya University, Coordination of Scientific Research Project (BAPK) under the contract no. 2009--50-02-023.

## References

[1] N. Samaele, P. Amornpitoksuk, S. Suwanboon, *Powder Technol.* **203**, 243 (2010).

[2] J. Zhao, C. Ye, X. Fang, L. Qin, L. Zhang, *Cryst. Growth Des.* **6**, 2643 (2006).

[3] J. Zhang, L. Sun, J. Yin, H. Su, C. Liao, C. Yan, *Chem. Mater.* **14**, 4172 (2002).

[4] P. Sagar, P.K. Shishodia, R.M. Mehra, *Appl. Surf. Sci.* **253**, 5419 (2007).

[5] Y.S. Kim, W.P. Tai, S.J. Shu, *Thin Solid Films* **491**, 153 (2005).

[6] S. Music, D. Dragevic, S. Popovic, M. Ivanda, *Mater. Lett.* **59**, 2388 (2005).

[7] S. Mridha, D. Basak, *Mater. Res. Bull.* **42**, 875 (2007).