

# Influence of pH on structural, optical and morphological properties of ZnO rod arrays fabricated by hydrothermal method

U. ALVER<sup>a,b\*</sup>, A. KUDRET, S. KERLI

<sup>a</sup>*Kahramanmaraş Sutcu Imam University, Department of Physics, 46100 Kahramanmaraş-Turkey*

<sup>b</sup>*Kahramanmaraş Sutcu Imam University, Research and Development Center for University-Industry, Public Relations (ÜSKİM), 46100 K. Maras-Turkey*

ZnO rod arrays have been grown on glass substrates with different pH by using a simple hydrothermal method at 95 °C without using a seed layer. Zinc nitrate hexahydrate ((Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was used as source of zinc ion, while hexamethylene tetramine (HMT, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>) solution served as the complexing agent. Ammonia (NH<sub>4</sub>OH) and acetic acid (CH<sub>3</sub>COOH) were used to achieve the desired pH value. No deposition is observed for the solution having pH values of 4 and 10. The effect of pH of precursor solution on structural, morphological and optical properties of ZnO rod arrays was investigated. XRD results indicate that the ZnO rods arrays are growing along [002] direction with a high consistent orientation perpendicular to the substrate. SEM images reveal that increase in the pH value from 5 to 9 leads to decrease in the size of rods grown on substrate. The optical measurements show that there is no significant change in the band gap of rod arrays with increasing the pH of the starting solution.

(Received May 18, 2011; accepted February 20, 2012)

**Keywords:** Hydrothermal growth, ZnO rod arrays, pH, Nanostructure

## 1. Introduction

One-dimensional (1D) ZnO nanostructures, such as nanorods, nanowires, nanobelts, and nanotubes have attracted a great research interest because of their scientific and technological applications [1–6]. ZnO is an n-type semiconductor ( $\Delta E_g=3.37$  eV) with a large exciton binding energy of 60 meV at room temperature. The properties of ZnO depend on preparative methods, chemical compositions and growth conditions. Much effort has been devoted to the development of ZnO nanostructures by different methods such as spray pyrolysis [7], chemical vapor deposition (CVD) [8], puls laser deposition [9], sputtering techniques [10,11] aqueous chemical and hydrothermal methods [12,13]. Among these methods, the hydrothermal method is promising for fabricating ideal nanomaterial with special morphology because of the simple, fast, less expensive, low growth temperature, high yield and scalable process.

Much research has been focused on the preparation and the properties of ZnO nanocrystals; however, little of it dealt with the pH effect of the solution on the crystallite size of ZnO powder. For instance, Li et al. [14] concluded that the solution conditions have a certain effect on the particle size of ZnO powders under hydrothermal conditions. Zhang et al. [15] found that the pH value can change the quantity of ZnO nuclei and of growth units. Lu and Yeh [16] found that the characteristics of ZnO powder profoundly depend on the pH of the starting solutions. In addition, the crystallinity and particle size of ZnO powder increase with a rise in the pH of solution. S.Baruah and

J.Dutta [17] studied the effect of pH variation on the dimension and morphology of zinc oxide (ZnO) nanorods grown through hydrothermal process at temperatures less than 100 °C on the pre-seed glass substrates.

These studies being mentioned in here are very limited, especially regarding the range of pH. In this work, ZnO rod arrays were deposited on glass substrates by hydrothermal process without using a seed layer but adjusting the pH of precursor solution from (acidic) to 10 (basic). The influence of pH on structural, morphological and optical properties of ZnO rod arrays films was investigated.

## 2. Experimental

ZnO rod arrays were grown by hydrothermal method from 0.01 M zinc nitrate hexahydrate ((Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and 0.01 M hexamethylene tetramine (HMT, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>) on glass slides which were cleaned by detergent and then completely rinsed in acetone and deionized water, respectively and dried in air. Initially, pH of as-prepared starting solution was measured as 6.5. Hydrothermal growth was carried out at 95 °C in a sealed beaker placed on a hotplate for 2 hours and then cooled down to room temperature. No seed layers were used to grow ZnO rod arrays. The prepared films were washed with distilled water and ethanol and finally dried at room temperature in air. The pH of starting solutions was adjusted to desired value using ammonia (NH<sub>4</sub>OH) and acetic acid (CH<sub>3</sub>COOH). The starting solution was prepared by adjusting pH (4, 5, 6.5, 7, 8, 9 and 10). No deposition is

observed on glass substrates for the solution having pH values of 4 and 10. Except pH values, all experimental conditions were kept the same for all samples.

The crystal structures of ZnO rod arrays were investigated by Philips X'Pert Pro X-ray diffractometer (XRD), with Cu  $K\alpha$  radiation, the surface morphologies were observed using a Jeol NeoScope JCM-5000 scanning electron microscopy (SEM) and the absorbance of the films in the visible region was measured using Shimadzu 1800 UV-Vis spectrophotometer.

### 3. Results and discussion

The pH of the precursor solution was found to play a major role in the deposition of ZnO rod arrays. At low pH values below 6.5 and at high pH values above 8, only poor quality deposition are produced. For the pH less than 5 and more than 9, no deposition was obtained. The reason for this should be higher reaction rate, when precipitates start to dissolve. Fig.1 presents the XRD patterns of ZnO crystal arrays deposited at different pH values on glass substrates. The XRD patterns of ZnO rod arrays at pH 4 and 10 are not obtained, due to any deposition on glass substrates. The patterns of the ZnO rod array films deposited on glass revealed three dominant peaks at  $2\theta=32.08^\circ$ ,  $34.73^\circ$  and  $36.65^\circ$  corresponding to (100), (002) and (101) planes, respectively. As shown, the strongest reflection observed along the (002) direction for all samples indicates that the ZnO rod arrays are preferentially well-oriented in the direction of the *c*-axis. As seen from Fig. 1, the intensities of the reflections peaks change as the pH increases from 5 to 9. The most intense peak of (002) is observed at 7 pH and the intensity of the (002) reflection peak was found to decrease as the pH increase to a value of 8 and 9. The decrease in intensity is linked to the poor crystallinity at high pH value, because the poor crystal quality for large pH values can be attributed to higher reaction rate, which was verified by the increasing of the precipitation rate of the solutions with increasing pH value. [18].

SEM images of the ZnO rod arrays grown with different pH value ranging from 5 to 9 are shown in Fig. 2. As can be seen SEM images, the orientation of the

obtained ZnO rod arrays strongly depends on the pH of the starting solution. Although no seed layers are on the substrates, it can be seen clearly that the samples produced from solution with 7, 8 and 9 pH consist of well-aligned nanorods with diameters varied from 200-300 nm, whereas the sample obtained without any reducing agents at 6.5 pH exhibits a random orientation with bigger size.

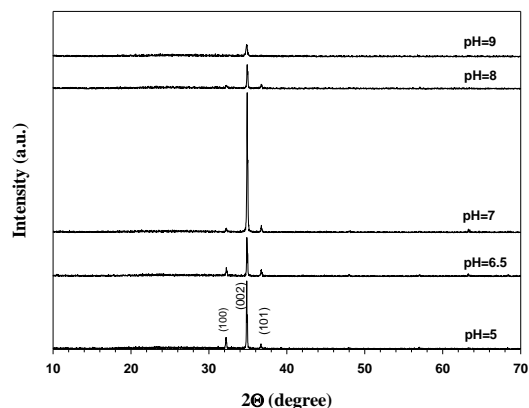


Fig. 1. XRD patterns of ZnO nanorod films at different pH values

The ZnO rod arrays obtained from solution with 5 pH were randomly oriented at low density on the entire substrate. For this sample, and the sample with 9 pH, the nucleation density was remarkably lower than that for ZnO rod arrays produced from solution with 6.5, 7, 8 and 9 pH. As mentioned earlier, for the sample having pH less than 5 and more than 9, no coating was observed. From SEM observations, it is clear that the morphological characteristics of as-prepared ZnO structures can be markedly controlled by the pH value of starting solution, even without using seed layer. In addition, as clearly seen from SEM images, although the shape of the structures remains the same, their overall dimensions change with increasing pH. In other words, one can tune-up the size of the ZnO structures from macro to nanorod by adjusting the pH of the solution.

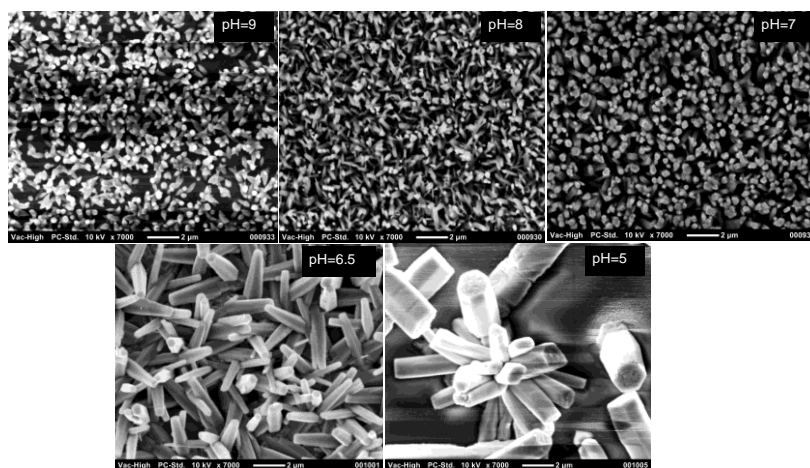


Fig. 2. SEM images of the ZnO nanorod films grown with different pH value.

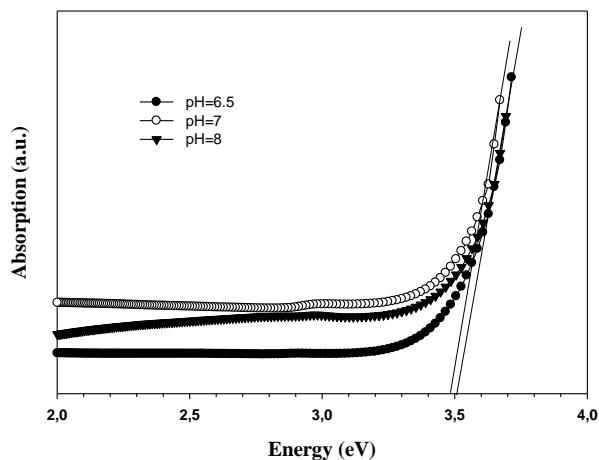


Fig.3. Absorption spectra of the ZnO nanorods with different pH value as a function of energy .

Fig. 3 shows the UV-Vis absorption spectra of the samples prepared at 6.5, 7, 8 pH versus the energy. Due to the partial substrate coverage, absorption spectra of the ZnO rod arrays prepared at 5 and 9 are not shown in Fig.3. The linear extrapolation of absorption curves towards the intersection with  $x$ -axis results in a direct band gap. These values changed from 3.51 to 3.48 eV with change in pH of the precursor solution from 6.5 to 8. These values are little higher than 3.37 eV which is generally reported in literature. This might be due to the small deposition thickness that might shift the band gap to a shorter wavelength. Moreover, although we expect the decrease in the optical band gap of the samples with increase in the pH of starting solution, we could not observe a significant variation of the optical transmission with pH. In general, it is known that the band gap energy varies in thin films due to particle size effect. The decrease in the optical band gap of the films with increase in the pH of starting solution could be attributed to the grain size enhancement, which takes place as a result of faster rate of hydrolysis and polycondensation in the films deposited from solution with higher pH.

#### 4. Conclusions

The ZnO rod arrays were grown on glass substrates with different pH by using a simple hydrothermal method without using seed layers. The size of the ZnO rod arrays was found to depend strongly on the pH value of precursor solution. From XRD and SEM observations it was concluded that the ZnO rod arrays can be grown from

microrod size to nanorod size by adjusting pH of precursor solution. Therefore, one can control the size of the ZnO crystal structures by adjusting the pH of the solution. In addition, due to higher precipitation rate, at pH 4 and 10 no film deposition was observed on glass slides. It was found out that pH does not influence too much the band gap energy of the ZnO rod arrays.

#### References

- [1] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* **292**, 1897 (2001).
- [2] Z. L. Wang, *J. Phys.: Condens. Matter* **16**, R829 (2004).
- [3] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang, *Nat. Mater.*, **4**, 455 (2005).
- [4] X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang, D. Zhu, *J. Am. Chem. Soc.*, **126**, 62 (2004).
- [5] X. Wang, C. J. Summers, Z. L. Wang, *Nano Lett.*, **4**, 423 (2004).
- [6] Z. R. Tian, J. A. Voigt, J. Liu, B. McKenzie, M. J. McDermott, M. A. Rodriguez, H. Konishi, H. Xu, *Nat. Mater.* **2**, 821 (2003).
- [7] M. T. Mohammad, A. A Hashim, M. H. Al-Maamory, *Mater. Chem. Phys.* **99**, 382 (2006).
- [8] S. T. Tan, B. J. Chen, X. W. Sun, X. Hu, X. H. Zhang, S. J. Chua, *J. Cryst. Growth* **281**, 571 (2005).
- [9] X. L. Guo, H. Tabata, *J. Cryst. Growth* **223**, 135 (2001).
- [10] W. T. Chiou, W. Y. Wu, J. M. Ting, *Diamond Relat. Mater.* **12**, 1841 (2003).
- [11] F. Quaranta, A. Valentini, F. R. Rizzi, G. Casamassima, *J. Appl. Phys.* **74**, 244 (1993).
- [12] B. Baruwati, D. K. Kumar, S. V. Manorama, *Sensors and Actuators B.* **119**, 676 (2006).
- [13] A. N. Baranov, C. H. Chang, O. A. Shlyakhtin, G. N. Panin, *Nanotechnology*, **15**, 1613 (2004).
- [14] W. J. Li, E. W. Shi, T. Fukuda, *Cryst. Res. Technol.* **38**, 847 (2003).
- [15] H. Zhang, D. Yang, X. Ma, Y. Ji, J. Xu, D. Que, *Nanotechnology*, **15**, 622 (2004).
- [16] C. H. Lu, C. H. Yeh, *Ceram. Int.*, **26**, 351 (2000).
- [17] S. Baruah, J. Dutta, *J. Cryst. Growth*, **311**, 2549 (2009).
- [18] S. Rani, P. Suri, P. K. Shishodia, R. M. Mehra, *Sol. Energy Mater. Sol Cells*, **92**, 1639 (2008).

\*Corresponding author: alver@ksu.edu.tr