

## Structural and Optical Properties of ZnO Thin Film Prepared by Oxidation of Zn Metal Powders

(Struktur and Ciri Optik Filem Nipis ZnO yang Disediakan Melalui Kaedah Pengoksidaan Serbuk Logam ZnO)

N.K. HASSAN & M.R.HASHIM\*

### ABSTRACT

*High quality ZnO nanostructures have been fabricated at room temperature by a simple vacuum thermal evaporator from metallic Zn powders (99.999% purity) on a silicon (100) substrate. The Zn thin films were then transferred into a thermal tube furnace for oxidation at 700°C for different time durations. Time was found to be a critical factor in the synthesis. This was followed by characterization of their morphological, structural and optical properties. The morphology of the grown ZnO nanostructures exhibited several large grains, which increased gradually with increasing oxidation time. The crystallinity of the grown nanostructures was investigated using X-ray diffraction, revealing that the synthesized ZnO was in hexagonal wurtzite phase. The photoluminescence (PL) spectra of the fabricated ZnO nanostructures showed high intensity peak in the UV region due to near-band-edge (NBE) emission in which the structures oxidized for 30 min showing highest intensity.*

*Keywords: Photoluminescence; vacuum thermal evaporator; ZnO nanostructures*

### ABSTRAK

*Struktur nano ZnO yang berkualiti tinggi telah difabrikasikan pada suhu bilik menggunakan teknik pengewap terma tervakum yang mudah daripada serbuk logam Zn (99.999% tulen) di atas substrat silikon (100). Filem nipis Zn kemudiannya dipindahkan ke dalam tiub relau pemanas untuk pengoksidaan pada suhu 700°C untuk masa yang berbeza. Masa pengoksidaan dikenal pasti sebagai sebagai faktor yang kritikal dalam sintesis. Ini diikuti oleh pencirian sifat-sifat permukaan, struktur dan optik. Permukaan struktur nano ZnO menunjukkan beberapa butiran yang besar, yang membesar apabila masa pengoksidaan ditingkatkan. Kehabluran struktur nano yang ditumbuh dikaji menggunakan pembelauan sinar-X, menunjukkan ZnO berada dalam fasa heksagonal wurtzite. Spektrum fotoluminesen (PL) struktur nano ZnO menunjukkan keamatan puncak yang tinggi di dalam rantau ultra-lembayung (UV) berpunca daripada pancaran daripada peralihan pinggir jalur dengan struktur teroksida pada 30 min menunjukkan pancaran paling tinggi keamatannya.*

*Kata kunci: Fotoluminesen; pengewap terma tervakum; struktur nano ZnO*

### INTRODUCTION

Due to its wide direct band gap (3.37 eV), large excitation binding energy (60 meV), excellent optical properties and low cost, zinc oxide (ZnO) has become one of the most important functional components in a plethora of devices, (Huang et al. 2001), solar cells (Chen et al. 2006), and gas sensors (Gupta et al. 2010; Kathirvel et al. 2009). Moreover, ZnO is a promising material for short wavelength optoelectronic devices, especially for ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes (LDs), due to its large exciton binding energy of 60 meV (Huang et al. 2001). The ZnO exciton binding energy is much larger than the room temperature thermal energy (26 meV), suggesting that the electron-hole pairs are stable even at room temperature. Therefore, efficient UV LEDs and LDs operating at room temperature can be expected, provided that high-quality p-type ZnO is available (Look 2005). Another advantage of ZnO is its low price, compared with other materials, placing it as a

promising candidate for industrial applications. ZnO thin films display three major photoluminescence peaks at around 378, 510 and 650 nm, corresponding to the colors of ultraviolet, green and red, respectively.

Many techniques have been employed to prepare ZnO films (Chang & Hung 2008; Gao et al. 2006; Hassan et al. 2011; Kong et al. 2003; Park et al. 2002; Tang et al. 2007; Wang 2004; Zhang 2010) including chemical vapor deposition, sol-gel, spray pyrolysis, molecular beam epitaxy, pulsed laser deposition, vacuum arc deposition and magnetron sputtering. Fabrication of ZnO films by thermal oxidation of Zn containing precursors, such as ZnS and Zn films, were also reported (Chen et al. 2006; Kitano et al. 1995; Kumar et al. 2011; Park et al. 2006). ZnO films synthesized using this method demonstrated excellent photoluminescence properties that were highly related to the applied temperature.

In the present work, ZnO films on silicon substrates were prepared by a simple oxidation of Zn films deposited

by vacuum thermal evaporation. Subsequently, the optical properties of the oxide films formed were studied.

#### EXPERIMENTAL DETAILS

High purity zinc powder (99.999% Sigma-Aldrich) was deposited on the substrate via thermal evaporation on n-type Si (100) substrate. A vacuum system using the diffusion pump with a base pressure of  $2.2 \times 10^{-4}$  torr was used for the deposition. In addition, metallic Zn powders were evaporated from the resistively heated tungsten boat. The Zn thin films were then successively transferred into a thermal tube furnace for oxidation at  $700^\circ\text{C}$  and  $\text{O}_2$  flow at 5 L/min at oxidation times of 10, 20 and 30 min to form the ZnO thin films. After the oxidation, the samples were cooled at room temperature.

The morphology of the formed ZnO nanostructures was observed with a scanning electron microscope (SEM, model JEOL JSM-6460LV with energy dispersive X-ray spectroscopy EDX installed). X-ray diffractometer (XRD; PANalytical X'Pert PRO diffractometer with  $\text{Cu K}\alpha$  radiation) was used for the structural measurements. The photoluminescence (PL) spectra of the samples were measured with a He-Cd laser (325 nm) at room temperature.

#### RESULTS AND DISCUSSION

Figure 1 shows the SEM photographs of ZnO films with various grain sizes. The surface morphology of the films varied with oxidation time. The grain size increased with increasing oxidation time, whereas the roughness of the samples decreased. This indicates that the films grown in three-dimensional (3D) and the rate of growth increased further until the maximum oxidation time of 30 min, leading to a smooth surface with uniform particles, as shown in Figure 1(c).

Figure 2 shows the XRD patterns of the thin films prepared at different oxidation times. All samples gave

similar XRD patterns, which indicate the high crystalline structure of the thin film. The synthesized ZnO thin films gave an XRD reflection peak detected at  $2\theta=34.4$ , indicating a (002) orientation. It is apparent that the  $2\theta$  value of the [0002] peak is almost typical to the standard value ( $2\theta = 34.43^\circ$ ) (Yogamalar et al. 2009). In addition, the intensity, as well as the full-width half-maximum of the (002) peak were observed to be dependent on the oxidation time. The ZnO peaks having much lower intensity were also detected at  $31.7$  and  $36.2$ , corresponding to the lattice planes (100) and (101), respectively. The ZnO peak of the film oxidized for 30 min is the highest and narrowest. The grain sizes ( $G_s$ ) of the ZnO films can be calculated using Scherer's formula (Kathirvel et al. 2009):

$$G_s = \frac{0.9\lambda}{B \cos \theta}, \quad (1)$$

where  $\lambda$ ,  $\theta$  and  $B$  are the X-ray wavelength (0.154 nm), the Bragg diffraction angle and the line-width at half-maximum of the (002) peak at around  $34.4$ , respectively. The calculated grain sizes of the samples were 29.4, 29.45 and 29.47 nm for the samples oxidized at  $700^\circ\text{C}$  for 10, 20 and 30 min, respectively. Obviously, the grain size of the samples increased with increasing oxidation time. This behavior was due to the relaxation of the strain. The as-grown film particles were under strain, thus, the relaxation of the strain enhances with increase in oxidation time.

Figure 3 shows the PL spectra of the samples prepared at oxidation times 10, 20 and 30 min. All the structures grown at different temperature zones showed a single strong, dominated and high-intensity peak in the UV region at 3.4, 3.37 and 3.38 eV. The UV emission is also referred to as the 'near-band-edge' emission, generated by the recombination of the free excitons through an exciton collision process (Huang et al. 2001; Ismardi et al. 2012; Jeong et al. 2003; Ye & Chen 2012). In addition, the improvement of crystal quality can cause a high-intensity near-band-edge emission with a very low or no green emission (Sekar et al. 2005). Based on the results, the UV

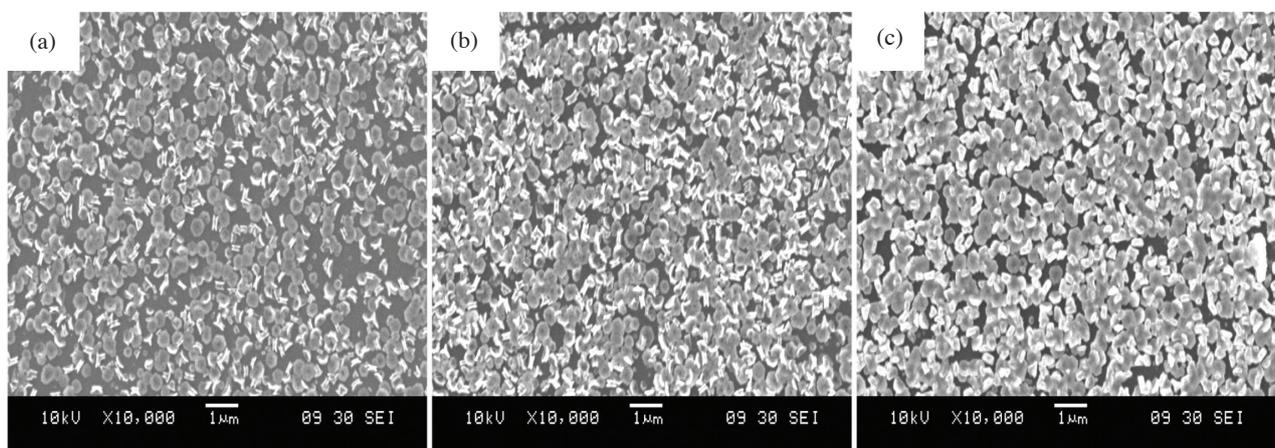


FIGURE 1. The typical surface SEM images of the samples prepared under different oxidation time of (a) 10, (b) 20 and (c) 30 min

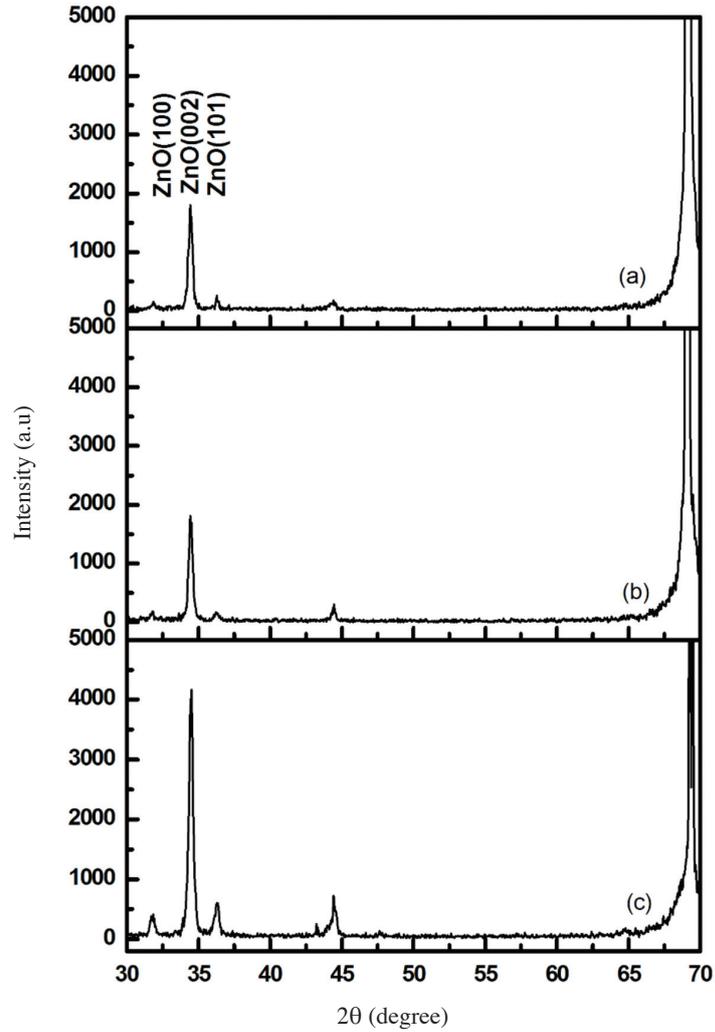


FIGURE 2. The XRD spectrum of the samples prepared under various oxidation time at (a) 10, (b) 20 and (c) 30 min

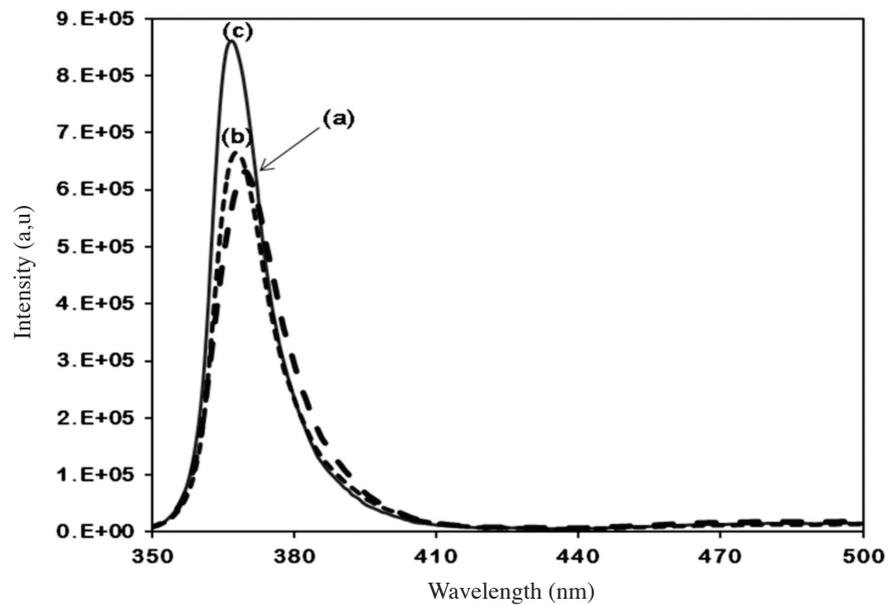


FIGURE 3. The PL spectra of the samples prepared at various oxidation times at (a) 10, (b) 20 and (c) 30 min in the UV region

peaks became more intensive at 30 min. No impurities and structural defects, such as oxygen vacancies and interstitials of zinc were observed.

In the synthesized ZnO nanoparticles grown on Si substrate, the near-band-edge emission dominated over the green-level emission, which indicates that the grown ZnO nanoparticles have good crystal quality with very little or no structural defects and that they display excellent optical properties.

#### CONCLUSION

A facile method was reported for the fabrication of highly crystalline ZnO nanostructure from metallic Zn via thermal evaporation technique. The morphology and crystallinity of the fabricated ZnO nanostructures were found to depend on the oxidation time. Extending the oxidation time from 10 to 20 min led to the growth of high crystalline ZnO nanostructures. Further increase in the oxidation time to 30 min resulted in the formation of large, smooth surface and uniform grains of ZnO nanostructure. XRD analyses showed that the ZnO nanostructure oxidized at 30 min have the best crystallinity. The photoluminescence (PL) measurements showed narrow peaks at the near-band-edge (NBE) emission which again confirms the high crystal quality of the fabricated nanostructure.

#### REFERENCES

- Chang, C.-J. & Hung, S.-T. 2008. Electrochemical deposition of ZnO pore-array structures and photoconductivity of ZnO/polymer hybrid films. *Thin Solid Films* 517: 1279-1283.
- Chen, Z.-G., Li, F., Liu, G., Tang, Y., Cong, H., Lu, G.Q. & Cheng, H.-M. 2006. Preparation of high purity ZnO nanobelts by thermal evaporation of ZnS. *J. Nanosci. Nanotechnol.* 6(3): 704-707.
- Chen, Z., Tang, Y., Zhang, L. & Luo, L. 2006. Electrodeposited nanoporous ZnO films exhibiting enhanced performance in dye-sensitized solar cells. *Electrochim. Acta.* 51: 5870-5875.
- Gao, Y.-F., Nagai, M., Masuda, Y., Sato, F. & Koumoto, K. 2006. Electrochemical deposition of ZnO film and its photoluminescence properties. *J. Cryst. Growth* 286: 445-450.
- Gupta, S.K., Joshi, A. & Kaur, M. 2010. Development of gas sensors using ZnO nanostructures. *J. Chem. Sci.* 122(1): 57-62.
- Hassan, J.J., Hassan, Z. & Abu-Hassan, H. 2011. High-quality vertically aligned ZnO nanorods synthesized by microwave-assisted CBD with ZnO-PVA complex seed layer on Si substrates. *J. Alloys Compd.* 509: 6711-6719.
- Huang, M.H., Mao, S., Feick, H., Yan, H., Wu, Y., Kind, H., Weber E., Russo, R. & Yang, P. 2001. Room-temperature ultraviolet nanowire nanolasers. *Science* 292(5523): 1897-1899.
- Huang, M.H., Wu, Y., Feick, H., Tran, N., Weber, E. & Yang, P. 2001. Catalytic growth of zinc oxide nanowires by vapor transport. *Adv. Mater.* 13(2): 113-116.
- Ismardi, A., Dee, C.F., Hamzah, A.A., Bais, B., Salleh, M.M., Majlis, B.Y. & Gebeshuber, I.C. 2012. Co-synthesis and characterization of In<sub>2</sub>O<sub>3</sub> and ZnO nanowires. *Sains Malaysiana* 41(4): 459-463.
- Jeong, S.-H., Kim, B.-S. & Lee, B.-T. 2003. Photoluminescence dependence of ZnO films grown on Si(100) by radio-frequency magnetron sputtering on the growth ambient. *Appl. Phys. Lett.* 82(16): 2625-2627.
- Kathirvel, P., Manoharan, D., Mohan, S.M. & Kumar, S. 2009. Spectral investigations of chemical bath deposited zinc oxide thin films - ammonia gas sensor. *J. of Optoelectronic and Biomedical Materials* 1(1): 25-33.
- Kitano, M., Okabe, T. & Shiojiri, M. 1995. Growth of electrocrystallized ZnO particles by reaction of vacuum-deposited Zn films with distilled water. *J. Cryst. Growth.* 152: 73-78.
- Kong, X., Sun, X., Li, X. & Li, Y. 2003. Catalytic growth of ZnO nanotubes. *Mater. Chem. Phys.* 82: 997-1001.
- Kumar, M.S., Chhikara, D. & Srivatsa, K.M.K. 2011. Structure-controlled growth of ZnO nanonails by thermal evaporation technique. *Cryst. Res. Technol.* 46(9): 991-996.
- Look, D.C. 2005. Electrical and optical properties of p-type ZnO. *Semicond. Sci. Technol.* 20: 55-61.
- Park, N.-K., Han, G.B., Lee, J.D., Ryu, S.O., Lee, T.J., Chang, W.C. & Chang, C.H. 2006. The growth of ZnO nano-wire by a thermal evaporation method with very small amount of oxygen. *Current Applied Physics* 6S1: 176-181.
- Park, W.I., Kim, D.H., Jung, S.-W. & Yi, G.-C. 2002. Metalorganic vapor-phase epitaxial growth of vertically well-aligned ZnO nanorods. *Appl. Phys. Lett.* 80(22): 4232-4234.
- Sekar, A., Kim, S.H., Umar, A. & Hahn, Y.B. 2005. Catalyst-free synthesis of ZnO nanowires on Si by oxidation of Zn powders. *J. Cryst. Growth* 277: 471-478.
- Tang, Y., Luo, L., Chen, Z., Jiang, Y., Bihui, L.A., Jia, Z. & Xu, L. 2007. Electrodeposition of ZnO nanotube arrays on TCO glass substrates. *Electroch. Commun.* 9: 289-292.
- Wang, Z.L. 2004. Zinc oxide nanostructures: Growth, properties and applications. *J. Phys. Condens. Matter.* 16: 829-858.
- Ye, N. & Chen, C.C. 2012. Investigation of ZnO nanorods synthesized by a solvothermal method, using Al-doped ZnO seed films. *Optical Materials* 34(4): 753-756.
- Yogamalar, R., Srinivasan, R., Vinu, A., Katsuhiko Ariga, & Bose, A.C. 2009. X-ray peak broadening analysis in ZnO nanoparticles. *Solid State Commun.* 149: 1919-1923.
- Zhang, C. 2010. High-quality oriented ZnO films grown by sol-gel process assisted with ZnO seed layer. *Journal of Physics and Chemistry of Solids* 71(3): 364-369.

Nano-optoelectronic Research Lab  
School of Physics  
Universiti Sains Malaysia  
11800 Penang  
Malaysia

\*Corresponding author; email: roslan@usm.my

Received: 7 January 2012

Accepted: 21 May 2012