

# Structural and optical properties of Al-doped ZnO nanowires synthesized by hydrothermal method

S.N. Bai <sup>a,\*</sup>, H.H. Tsai <sup>b</sup>, T.Y. Tseng <sup>b</sup>

<sup>a</sup> Department of Electronic Engineering, Chienkuo Technology University, Changhua 500, Taiwan, ROC

<sup>b</sup> Department of Electronics Engineering and Institute of Electronics, National Chiao-Tung University, Hsinchu 300, Taiwan, ROC

Available online 18 June 2007

## Abstract

The growth of one dimensional Al-doped ZnO nanowires on a silicon substrate with a ZnO seeding layer by using a low temperature hydrothermal method is demonstrated. The structural and optical characteristics of the solution-grown Al-doped ZnO nanowires were studied using field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and cathodoluminescence (CL) measurements. The FE-SEM images show that the ZnO nanowires are hexagonal column shaped and stand perpendicularly on the silicon substrate. It is found in XRD patterns that the ZnO nanowires annealed at various temperatures are all wurtzite crystal structure and have (002) preferred orientation. As the annealing temperature changed, the intensity of (100) and (101) peaks reveals distinct change. The CL spectra show the as-grown ZnO nanowires display a weak and narrow UV emission centered at 376 nm. A strong and very broad green–yellow emission band with a center at 575 nm as well as a shoulder like orange–red emission band centering at 625 nm is also demonstrated. It is shown that the luminescence intensity centered at 376 nm increased, the shoulder like emission centered at 625 nm decreased but emission centered at 575 nm disappeared after thermal annealing treatment in oxygen atmosphere.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** ZnO nanowire; Structural properties; Optical properties; Hydrothermal method

## 1. Introduction

Recently, Zinc oxide (ZnO) has been attracting particular interest because of its remarkable optical and electronic properties. Its significant optical transparency combined with an excellent electrical conductivity made ZnO as a promising material for the fabrication of optoelectronic devices [1–4]. ZnO is an n-type wide direct bandgap oxide semiconductor material with a bandgap energy of 3.3 eV and high exciton binding energy of 60 meV, and also good stability in ambient environments. One-dimensional (1D) ZnO nanowires are extensively being considered as the candidate materials for field emission, ultraviolet lasing and blue light-emitting devices. Many investigations have been made on both preparation and application of 1D ZnO nanowires [5–7]. The investigation to grow well-aligned nanowire array is a very

important issue because it is a key process toward realizing nanoscale devices. In this study, we report the two-step hydrothermal method for synthesizing uniform and ordered ZnO nanowires on silicon substrates. The nanowires were grown in a highly vertically aligned manner by a textured ZnO seeding layer on the silicon substrate. Effects of the growth condition and post heat treatment on the structural and optical characteristics of ZnO nanowires were studied.

## 2. Experimental

Aluminum (Al) doped ZnO nanowires were grown on silicon (Si) substrate by using seed-assisted hydrothermal method. The p-type Si substrate (100) was cleaned using a standard Radio Corporation of America (RCA) cleaning method and rinsed in acetone for 30 min to remove pollutants from the surface of the silicon substrate. The Al thin film (850 nm) was then deposited on the Si substrate by thermal evaporation as the n-type doped material. After deposition of the Al thin film, there was a 40 nm thick seeding layer of ZnO grown by R.F. magnetron sputtering and in-situ annealing at

\* Corresponding author.

E-mail addresses: [snbai@cc.ctu.edu.tw](mailto:snbai@cc.ctu.edu.tw) (S.N. Bai), [tseng@cc.nctu.edu.tw](mailto:tseng@cc.nctu.edu.tw) (T.Y. Tseng).

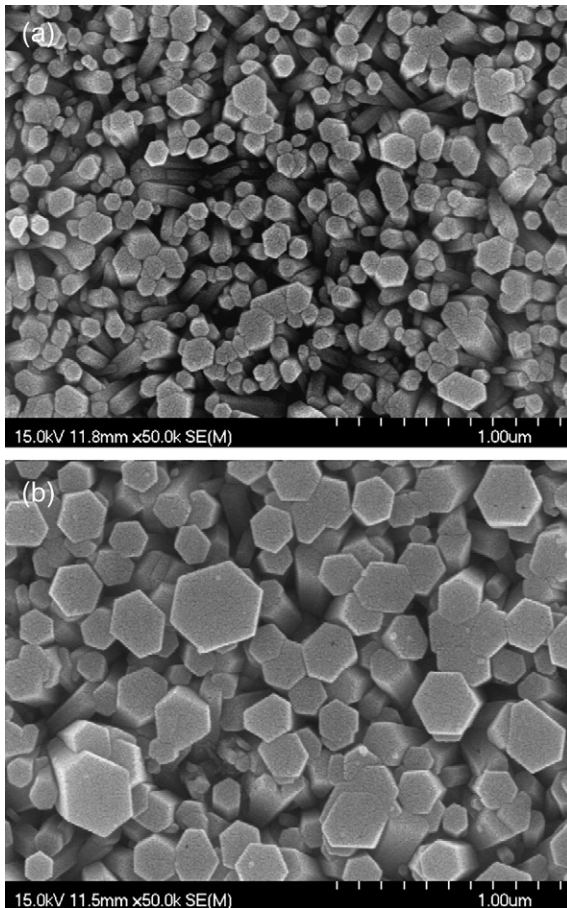


Fig. 1. SEM images of Al-doped ZnO nanowires annealed in the oxygen atmosphere at 550 °C for (a) 1 h (b) 7 h.

550 °C for 3 h. Then, the Si substrate with Al thin film and ZnO seeding layer was placed in an aqueous solution of zinc nitrate hexahydrate (99.9% purity) and hexamethylenetetra-mine (99.9% purity) in a 95 °C sealed vessel for 3h. The solution concentration of zinc and amine was fixed at 0.1 M. After the ZnO nanowires were formed, Al was diffused from Al thin film layer into the ZnO nanowires by employing the thermal diffusion method under temperature range from 550 to 650 °C for 1 to 7 h in oxygen atmosphere.

The morphology and microstructure of the ZnO nanowires were investigated by field emission scanning electron microscopy (FE-SEM). The crystalline structure and orientation of the ZnO nanowires were identified by X-ray diffractometry (MAC Science, MXP18, Japan) using  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The Al content in the ZnO nanowires was determined by energy dispersive X-ray analysis (EDX). The optical properties measurement was performed using the cathodoluminescence (CL) with an electron beam as an excitation source (15 kV) at room temperature.

### 3. Results and discussion

Fig. 1(a) and (b) show the FE-SEM micrographs of ZnO nanowires annealed at 550 °C for 1 and 7 h, which display that the nanowires are straight with smooth top and hexagon-shaped

columnar structure, providing explicit proof that the nanowires grow along the *c*-axis direction. The nanowire diameter observed from SEM images ranges from 80 to 210 nm. There is no apparent change in the length for the nanowires after annealing at 550 °C for 7 h. Moreover, it is revealed that average diameter of the nanowires increases as the growth time increases and there is a simultaneous increase in ZnO nanowire agglomeration.

Fig. 2(a)–(c) show the X-ray diffraction (XRD) patterns of the ZnO nanowires annealed in oxygen atmosphere at

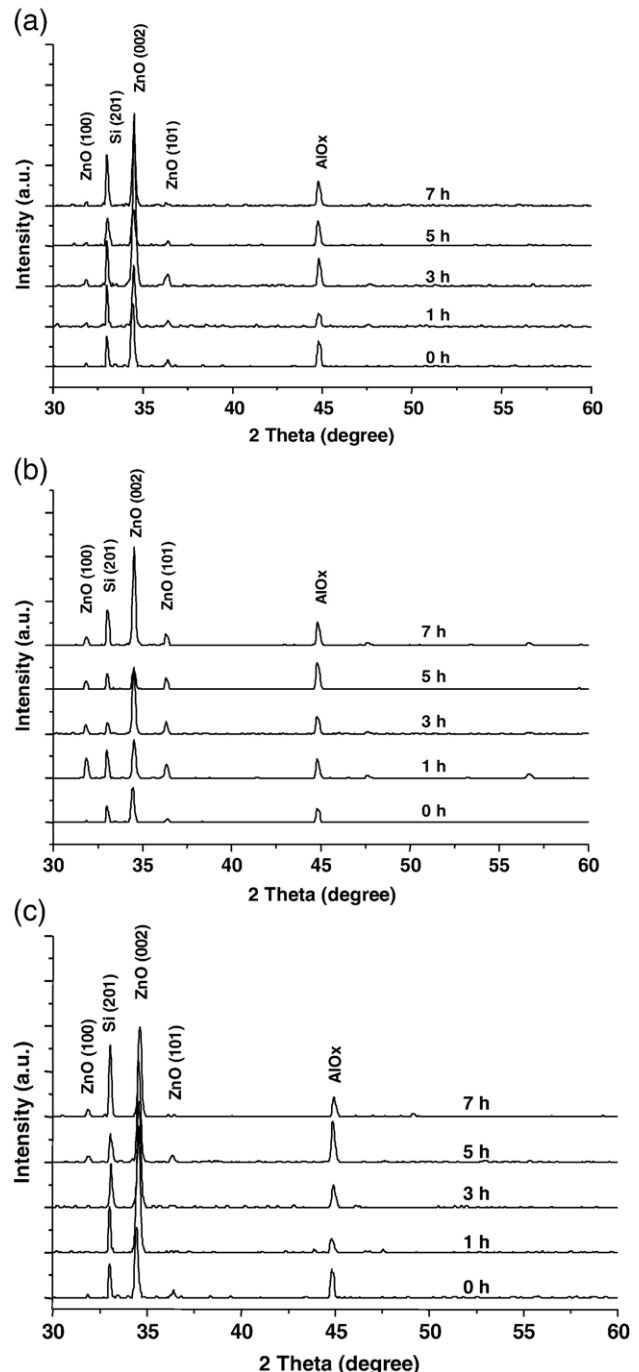


Fig. 2. X-ray diffraction patterns of Al-doped ZnO nanowires annealed in oxygen atmosphere at (a) 550 °C (b) 600 °C (c) 650 °C.

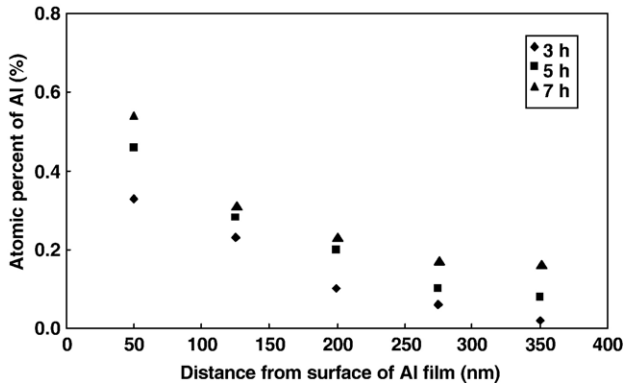


Fig. 3. Atomic percentage of Al in the ZnO nanowires annealed at 550 °C in oxygen atmosphere at various distances from the Al thin films under different thermal annealing times.

temperatures 550, 600 and 650 °C for various times indicated. All of the diffraction peaks can be identified as wurtzite structured ZnO (JCPDS card No. 36-1451), except those marked with Si and AlO<sub>x</sub> coming from silicon substrate and aluminum dopant. No characteristic peaks from other impurities are detected. It is shown that some amount of aluminum dopant might be segregated as AlO<sub>x</sub> in the nanowires. Prior to ZnO nanowires growing, the seeding layer shows excellent preferred (002) reflection (not shown here), suggesting the seeding layer has *c*-axis-preferred orientation perpendicular to the substrate surface. Those grown ZnO nanowires exhibit sharp XRD patterns due to the high degree of crystallization. The most intensive peak presented is shown as (002) plane and additional peaks along with (100) and (101) planes are also observed. In addition, the intensity of (100) and (101) peaks decrease with increasing thermal annealing temperature. The higher annealing temperature significantly improves the crystallization of the ZnO nanowires and enhances the grain size.

Fig. 3 demonstrates the EDX analysis results of the Al diffusion ratio ( $C_x/C_s$ ) between Al thin film layer and ZnO nanowires where  $C_s$  represents the atomic percent of Al in the

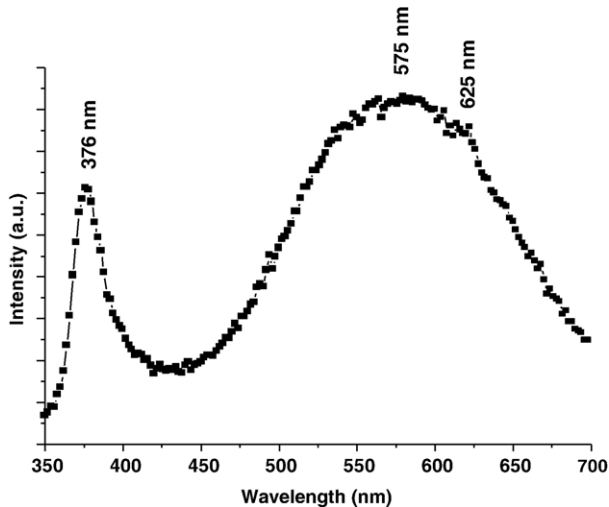


Fig. 4. Cathodoluminescence spectrum of the pure ZnO nanowires.

Al thin film layer and  $C_x$  represents the atomic percent of Al in the ZnO nanowires away  $x$  distance from the surface of Al thin film layer. The Al diffusion ratio increases as the thermal annealing time increases and decreases with increasing  $x$  distance. The post thermal annealing process results in doping Al into the ZnO nanowires and then the incorporated Al occupying the zinc sites in the nanowires, leading to higher charge carrier density and lower electrical resistivity [1].

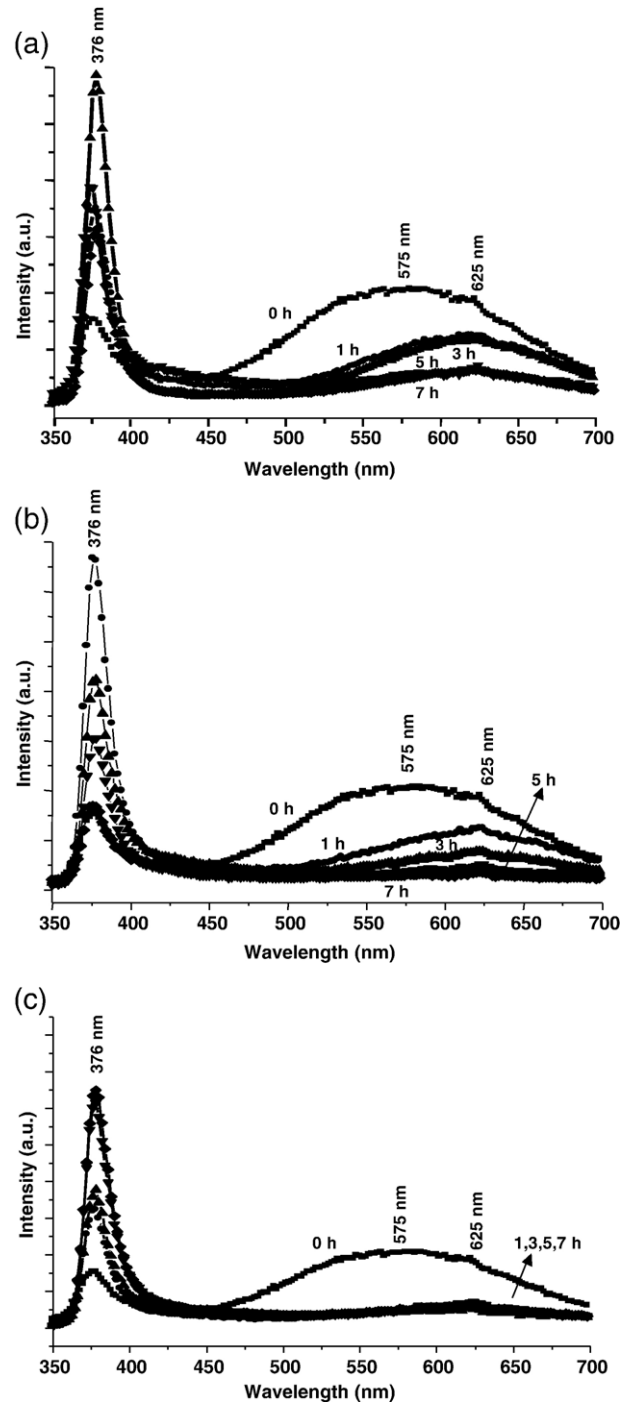


Fig. 5. Cathodoluminescence spectra of Al-doped ZnO nanowires under various thermal annealing times in the oxygen atmosphere at (a) 550 °C (b) 600 °C (c) 650 °C.

Fig. 4 shows the CL spectrum for the as-grown ZnO nanowires excited by the electron beam, indicating UV and visible CL spectra. A relatively weak and narrow UV emission band is observed around 376 nm. In addition, a much stronger and broader emission band is located in the green–yellow part of the visible spectrum with an emission peak about 575 nm. Besides these two strong emission peaks, a very weak orange–red emission centering at about 625 nm is also shown.

It is well known the stoichiometric ZnO structure generally exhibits intense UV luminescence. The origin of the near-UV luminescence is attributed to the excited electron emitted from the conduction band to valence band [8]. That is, the peak (376 nm) is due to the exciton emission from conduction band to valence band, which is an intrinsic property of ZnO. Furthermore, it is reasonable to assume that the visible luminescence (575 nm and 625 nm) in this study occurs primarily resulted from the intrinsic or extrinsic defects. The intrinsic defects are associated with deep level emissions such as oxygen vacancies, zinc interstitials, zinc vacancies, oxygen interstitials, or oxygen antisites [9]. Moreover, the extrinsic defects are likely to have resulted from absorbed water or surface hydroxyl groups [10–12]. The as-grown ZnO nanowires prepared by solution-phase growth at low temperature usually have high defect concentrations and typically demonstrate weak UV but significant defect emissions at room temperature [13]. According to the previous reports, the origin of green–yellow emission around 575 nm is likely to have resulted from the absorbed water or surface hydroxyl (OH) groups [10–12] while the orange–red emission at about 625 nm is probably related to the oxygen interstitials [14–16].

Fig. 5 shows the CL spectra of the Al-doped ZnO nanowires annealed at various temperatures in an oxygen atmosphere. The analysis of CL emission can be used to study the defect characteristics of ZnO nanowires by heat treatment at different times and temperatures in various oxygen partial pressures. In this method, the defects can be varied and then related to changes in the emission intensity.

From Fig. 5, it can be observed that the annealing temperature and time have significant influences on the optical properties of the ZnO nanowires. The UV emission peak of ZnO nanowires is significantly increased comparing with the visible emission peaks with increasing annealing temperature. Both UV and visible emissions demonstrate a negligible peak shift with increasing temperature. Additionally, the green–yellow emission centering at about 575 nm disappears and the orange–red emission centering at about 625 nm is decreased as the annealing time increased. This feature is most likely due to an increase of desorption of absorbed water/surface hydroxyl groups and a decrease of the density of oxygen interstitial with increasing thermal annealing temperature.

#### 4. Conclusions

Highly dense arrays of Al-doped ZnO nanowires have been grown on Si substrates with a simple and efficient two-step method. The ZnO nanowires were prepared using an R.F. sputtered ZnO seeding layer followed by a hydrothermal growth

method. The analysis of SEM images and XRD pattern illustrates that the nanowires are preferentially aligned in the *c*-axis of the ZnO wurtzite-type structure and vertical to the Si substrate. The CL spectra show that the ZnO nanowires have two clear emission bands and one ambiguous emission band. For the two clear emission bands, one is a relatively weak and narrow UV emission centered about 376 nm that is widely accepted due to the exciton emission from conduction band to valence band and the other is a much stronger and broader emission observed in the green–yellow range of the visible spectrum with an emission peak about 575 nm that is believed to be caused by extrinsic impurities such as absorbed water or surface hydroxyl groups. In addition to these two clear emission peaks, a very weak orange–red emission centering at about 625 nm is shown, which is most probably resulted from the oxygen interstitials. The CL measurements also reveal that the strong visible emission located in the green–yellow range disappeared and replaced by strong UV emission after thermal annealing treatment. These well-aligned arrays of ZnO nanowires are ongoing to study and expected to be a multifunctional constituent for field emission display, solar cells, and other electronic devices due to their unique electrical and optical properties.

#### Acknowledgement

The authors gratefully appreciate the financial support from the National Science Council of Republic of China under Project Numbers NSC 95-2221-E-009-120 and NSC 95-2221-E-270-018.

#### References

- [1] S.N. Bai, T.Y. Tseng, Thin Solid Films 515 (2006) 872.
- [2] J. Hupkes, B. Rech, S. Calnan, O. Kluth, U. Zastrow, H. Siekmann, M. Wuttig, Thin Solid Films 502 (2006) 286.
- [3] H. Nanto, T. Minami, S. Shooji, S. Takata, J. Appl. Phys. 55 (1984) 1029.
- [4] X. Jiang, F.L. Wong, M.K. Fung, S.T. Lee, Appl. Phys. Lett. 83 (2003) 1875.
- [5] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science 292 (2001) 1897.
- [6] S.Y. Li, P. Lin, C.Y. Lee, T.Y. Tseng, J. Appl. Phys. 95 (2004) 3711.
- [7] C.Y. Lee, S.Y. Li, P. Lin, T.Y. Tseng, IEEE Trans. on Nanotechnology 5 (2006) 216.
- [8] D.C. Reynolds, D.C. Look, B. Jogai, J.E. Hoelscher, R.E. Sherriff, M.T. Harris, M.J. Callahan, J. Appl. Phys. 88 (2000) 2152.
- [9] Y.P. Wang, W.I. Lee, T.Y. Tseng, Appl. Phys. Lett. 69 (1996) 1807.
- [10] R. Xie, D. Li, D. Yang, T. Sekiguchi, M. Jiang, Nanotechnology 17 (2006) 2789.
- [11] K.H. Tam, C.K. Cheung, Y.H. Leung, A.B. Djuricic, C.C. Ling, C.D. Beling, S. Fung, W.M. Kwok, W.K. Chan, D.L. Phillips, L. Ding, W.K. Ge, J. Phys. Chem., B 110 (2006) 20865.
- [12] N.S. Norberg, D.R. Gamelin, J. Phys. Chem., B 109 (2005) 20810.
- [13] D. Li, Y.H. Leung, A.B. Djuricic, Z.T. Liu, M.H. Xie, S.L. Shi, S.J. Xu, W.K. Chan, Appl. Phys. Lett. 85 (2004) 1601.
- [14] S.A. Studenikin, N. Golego, M. Cocivera, J. Appl. Phys. 84 (1998) 2287.
- [15] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong, Appl. Phys. Lett. 78 (2001) 2285.
- [16] Y.G. Wang, S.P. Lau, H.W. Lee, S.F. Yu, B.K. Tay, X.H. Zhang, H.H. Hng, J. Appl. Phys. 94 (2003) 354.